

205. *The Extraction of Chromium(VI) from Aqueous Solution by Tri-n-butyl Phosphate.*

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The extraction of chromium(VI) into tri-n-butyl phosphate from aqueous perchloric, sulphuric, nitric, hydrochloric, and hydrobromic acid has been studied at both tracer and macro-concentrations. With hydrochloric and hydrobromic acid, the species in the organic phase is HCrO_3X ($\text{X} = \text{Cl}, \text{Br}$); in the other acids, the organic phase contains $\text{H}_2\text{Cr}_2\text{O}_7$. The number of solvent molecules solvating the extracted species in the organic phase has been measured; the values found are discussed in terms of the H_9O_4^+ ion.

A NUMBER of papers in the literature have been concerned with the extraction of chromium(VI) from aqueous solution by basic organic solvents, especially for analytical purposes. Solvents used include 4-methylpentan-2-one ("hexone")¹⁻⁴ and diethyl ether.⁵ It should be emphasised immediately that the statement made by Weinhardt and Hixson,¹ that 4-methylpentan-2-one is a selective solvent for chromium(VI), is incorrect, both in the sense that chromium(VI) species can be extracted by a number of different basic organic solvents, and equally in that 4-methylpentan-2-one is known to extract many other elements. Various authors have reported the use of phosphorus-containing solvents for this extraction. White and Ross⁶ used trioctylphosphine oxide for the extraction of macro-amounts of chromium, and Specker and Arend⁷ and Shevchenko, Shilin, and Zhdanov⁸ have discussed various aspects of the extraction by tri-n-butyl phosphate, a solvent which is of special interest because of its use in the industrial processing of nuclear fuels.

The extraction of chromium(VI) has a number of peculiar features, arising from the multiple pH-dependent equilibria in the aqueous phase. In particular, two dibasic acids, chromic and dichromic, can in principle be extracted by basic solvents. We have studied the extraction of macro- and tracer amounts of chromium(VI) from hydrochloric, hydrobromic, sulphuric, perchloric, and nitric acid media by both pure tributyl phosphate and its solutions in an inert solvent (cyclohexane). In general, the results do not completely confirm some of the previous views on the mechanism of the extraction; also, additional equilibria involving chromium(VI) in the aqueous phase may now have to be postulated.

EXPERIMENTAL

Materials.—Chromium trioxide and potassium dichromate were both of analytical grade; recrystallised sodium dichromate dihydrate was used without further purification. Reagent grade acids were used as supplied, except for hydrobromic acid which was shaken with 5% tributyl phosphate in chloroform to remove any traces of free bromine or HBr_3 . Water was ion-exchanged water which, for certain experiments, was distilled from alkaline permanganate.

Tri-n-butyl phosphate was normally purified by the method described previously;⁹ that used in tracer experiments was also pretreated with permanganate to remove any reducing impurities. Cyclohexane (May and Baker) was used without further treatment.

Procedure.—In experiments involving macro-quantities of chromium, initially equal volumes (3–20 ml.) of aqueous and organic phases were shaken together in stoppered glass tubes. With hydrochloric, hydrobromic, or sulphuric acid aqueous phases, the time factor was unimportant, but with perchloric or nitric acid media, the extraction and separation had to be

¹ Weinhardt and Hixson, *Ind. Eng. Chem.*, 1951, **43**, 1676.

² Bryan and Dean, *Analyt. Chem.*, 1957, **29**, 1289.

³ Dean and Beverly, *Analyt. Chem.*, 1958, **30**, 977.

⁴ Blundy, *Analyst*, 1958, **83**, 555.

⁵ Bock and Bock, *Z. anorg. Chem.*, 1950, **263**, 146.

⁶ White and Ross, ORNL-2326.

⁷ Specker and Arend, *Naturwiss.*, 1961, **48**, 524.

⁸ Shevchenko, Shilin, and Zhdanov, *J. Inorg. Chem. (U.S.S.R.)*, 1960, **5**, 1367.

⁹ Tuck, *J.*, 1958, 2783.

carried out as quickly as possible to minimise the reduction of chromium(VI) in the organic phase.

The composition of the initial aqueous solution was fixed by dissolving known weights of potassium dichromate in *n*-solutions of the appropriate acid (except that with perchloric acid sodium dichromate was used because of the low solubility of potassium perchlorate). The equilibrium aqueous phase was analysed volumetrically to determine the final acid, chromium(VI), and anion content. The amount extracted into the organic phase could only be determined by subtraction, since the organic solvents usually used to achieve homogeneity with water (*e.g.*, neutralised aqueous acetone) are all readily oxidised by chromium(VI) in the presence of mineral acids.

Radioactive Tracer Experiments.—Chromium-51 ($t_{1/2}$ 28 days) was supplied (Radiochemical Centre, Amersham) as a solution of chromium(III) in dilute perchloric acid. Carrier (CrO_3) was added so that the final chromium(VI) concentration would be 5 mM. After addition of carrier, the solution was oxidised with alkaline hydrogen peroxide; excess of oxidising agent was decomposed by boiling, and the solution was acidified with the appropriate mineral acid. The acid solution was next equilibrated with tributyl phosphate; the organic phase was removed, after centrifuging, and the extracted chromium(VI) back-washed into an aqueous solution. Dilution of the tributyl phosphate with cyclohexane served to increase the amount of chromium removed into aqueous solution. This extraction cycle ensured that tracer and carrier were in the same chemical state, and also that all the tracer was present as chromium(VI), since chromium(III) is not extracted by tributyl phosphate under the conditions used (see also ref. 8).

The distribution coefficient (D_{Cr}) of chromium was determined by counting the activity of equal volumes of organic and aqueous phases, with a Philips thallium-activated sodium iodide scintillation counter and γ -spectrometer set to count only the 0.323 Mev γ -ray of ^{51}Cr ; then

$$D_{\text{Cr}} = \frac{{}^{51}\text{Cr activity (counts/min./ml.), organic phase}}{{}^{51}\text{Cr activity (counts/min./ml.), aqueous phase}}$$

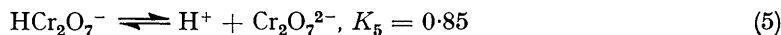
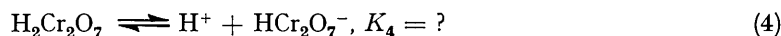
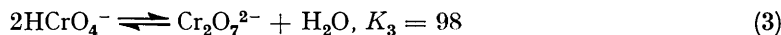
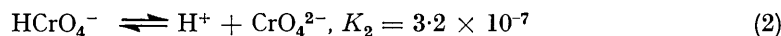
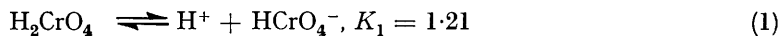
Absorption Spectra.—The ultraviolet and visible spectra were measured over the range 50,000—13,000 cm^{-1} with a Unicam S.P. 700 recording spectrophotometer.

pH Experiments.—A series of experiments was carried out to determine the effect of the pH of the equilibrium aqueous phase on the chromium(VI) distribution coefficient. The aqueous phase was made up from perchloric acid-sodium perchlorate mixtures to give 0.1M constant ionic strength. A Marconi pH-meter with a glass electrode was used for pH determinations. Preliminary experiments were carried out to establish the correct initial conditions to give the required equilibrium pH.

In order to keep the chromium concentration as low as possible, a solution of $\text{Na}_2^{51}\text{CrO}_4$ in isotonic saline was diluted with perchloric acid, without adding chromium carrier; calculations showed that the amount of chloride ion in the final solutions was of the same order as that present from the "AnalaR" perchloric acid used.

RESULTS AND DISCUSSION

Chromium(VI) Species in Aqueous Solution.—The various equilibria which may be established in the aqueous phase are shown in (1)—(5). The values quoted for the equilibrium constants were obtained by glass-electrode¹⁰ or spectrophotometric^{11,12} methods.



¹⁰ Neuss and Rieman, *J. Amer. Chem. Soc.*, 1934, **56**, 2238.

¹¹ Tong and King, *J. Amer. Chem. Soc.*, 1953, **75**, 6180.

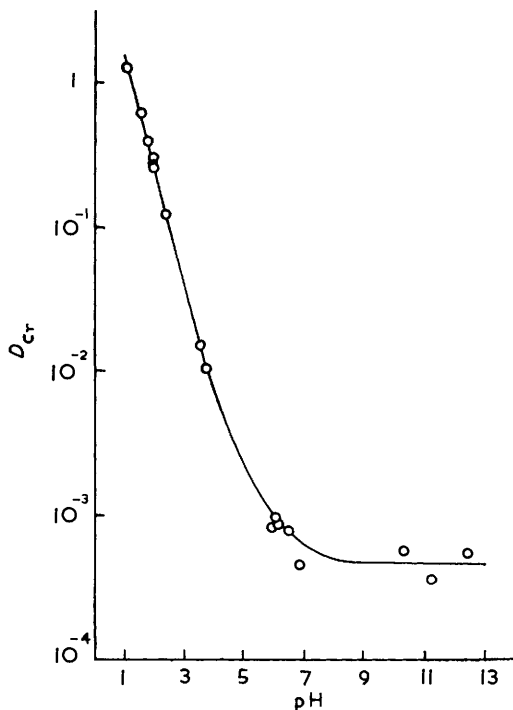
¹² Davies and Prue, *Trans. Faraday Soc.*, 1955, **51**, 1045.

Some, at least, of these constants vary with ionic strength,¹² but this does not affect the present arguments.

As tri-*n*-butyl phosphate is a strongly basic solvent, one would expect only acidic species to be extracted from aqueous solution. The factors affecting the extraction of acids by such solvents have been discussed elsewhere;¹³ the model presented implies that the main factors involved are acid strength, anion size, and the hydrophilic (or hydrophobic) nature of the anion. The present results agree with this model as far as it can be applied.

In view of the subsequent discussion, it is unfortunate that no value is available for K_4 , the first ionisation constant of dichromic acid. Tong and King¹¹ point out however that for complex oxyacids of non-transition metals, the ratio K_{i_1}/K_{i_2} is of the order of 10^4 , whereas the corresponding ratio for chromic acid ($K_{H_2CrO_4}/K_{HCrO_4^-}$) is actually 2×10^6 ;

FIG. 1. D_{Cr} as a function of pH at 0.1M constant ionic strength.



if this argument can be extended to dichromic acid for which K_{i_2} ($=K_5$ above) = 0.85, the first ionisation constant is $\sim 10^6$. If this figure is correct even within a few orders of magnitude, we are dealing with a system in which there are two possible chromium oxyacids, one strong and the other very strong (in terms of K_{i_1}), of which the stronger is obviously much the larger.

Dependence of Extraction on pH.—The variation of the chromium(vi) distribution coefficient with the pH of the equilibrium aqueous phase over the pH range 1–13 is shown in Fig. 1. These results show that the extraction from basic or neutral solution is extremely low; in fact the chromium-51 activity in the organic phase in this region was only a few counts/min. above background, and the scatter of the experimental points can be ascribed entirely to the low statistical accuracy of the results in these circumstances.

The importance of acidic species in the extraction mechanism is clear, and we can eliminate immediately the possibility that sodium chromate or dichromate is extracted

¹³ Tuck, J., in the press.

by the organic phase.* In agreement with this, the amount of sodium detected by flame-photometry in an aliquot portion of tributyl phosphate equilibrated with $\sim 0.05M$ -sodium dichromate in *m*-perchloric acid was less than 1 p.p.m.; comparison with other results showed that over 100 p.p.m. would have been found if sodium dichromate had been the extracted species.

The chromium(VI) concentration in the initial aqueous phase in these experiments was $6.8 \times 10^{-7}M$, so that, at all pH's below 6, the species present must be predominantly $HCr_2O_7^-$ (the equilibrium constants quoted above being used). In agreement with this,

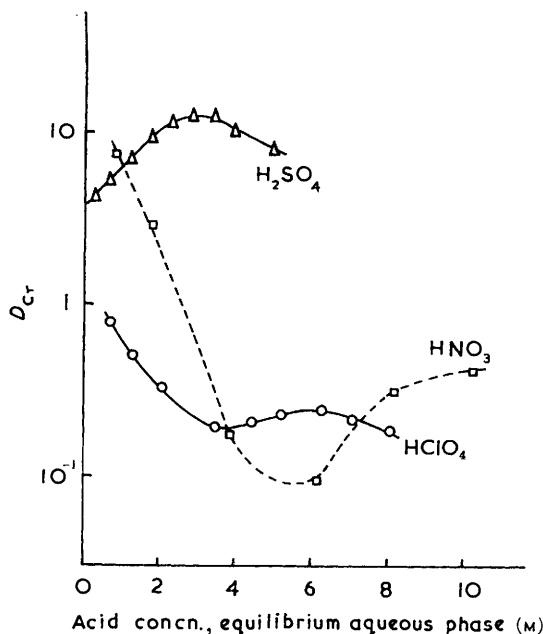


FIG. 2. D_{Cr} as a function of acid concentration for sulphuric, nitric, and perchloric acid solutions.

over the pH range 1.5–4, D_{Cr} is a linear function of pH. This can be shown to arise from the process (6) (TBP = tributyl phosphate)



for which

$$K_6 = \frac{[\text{complex}_o]}{[HCr_2O_7^-][H^+][TBP]^n},$$

so that

$$D = \frac{[\text{complex}_o]}{[HCr_2O_7^-]_{aq}} = \text{const.} [H^+]$$

at constant $[TBP_o]$. At higher acidities, this argument no longer holds because of the significant amount of perchloric acid which is extracted by the organic phase, thus affecting the concentration of "free" tributyl phosphate at equilibrium. The non-linearity at lower hydrogen-ion concentrations is of course related to the establishment of various equilibria set out in eqns. (1)–(5). In principle the equilibrium constants for some of these could be calculated from the results in Fig. 1, were it not for the fact that the partition coefficient (as defined in ref. 14) for dichromic acid cannot be obtained experimentally.

Tracer Extraction from Mineral Acids.—The distribution coefficients (D_{Cr}) for the extraction of chromium(VI) by tributyl phosphate from sulphuric, nitric, and perchloric acid solutions, initially $\sim 10^{-3}M$ in chromium, are shown in Fig. 2. With hydrochloric

* Shevchenko *et al.*⁸ seem to imply that " $K_2Cr_2O_7$ was extracted from 1M- $HClO_4$ and 3M- HNO_3 ," but this may be merely unfortunate wording of the translation, since their arguments involve only acidic species in the organic phase.

¹⁴ Diamond and Tuck, *Progr. Inorg. Chem.*, 1960, 2, 109.

and hydrobromic acid, extraction was complete within experimental error up to about 4M concentrations of aqueous phase acid at equilibrium. Above these acidities, the aqueous phase at equilibrium always showed traces of green chromium(III) species, arising from reduction by the solvent. Since, however, later work showed that the extracted species from these two acids is not the same as that from sulphuric, nitric, and perchloric acid, the lack of comparable data is not important. It is of course not completely certain that the results shown in Fig. 2 are unaffected by reduction, although care was taken to carry out the experiments as quickly as possible to minimise any such effect.

In fact, the results shown agree with the explanation given by Diamond¹⁵ for the extraction of InCl_4^- . Thus, because of the "common ion" effect in the organic phase, acids which are themselves extracted well and which dissociate in the organic phase depress the extraction of the chromium(VI) acidic species. Both nitric and perchloric acid fulfil these conditions, so that, as their concentration increases, D_{Cr} falls, and in fact the curves in Fig. 2 correlate well with those for the extraction of nitric and perchloric acid by tributyl phosphate.¹³ A second effect discussed by Diamond explains the slower rise at higher acidities, namely the lowering of the water activity, which tends to force species into the organic phase by reducing the hydration forces in the aqueous phase. This is shown quite clearly by nitric, and to a lesser extent by perchloric acid; the final slight fall in D_{Cr} in concentrated perchloric acid may be due to perchloric acid competing successfully with dichromic acid for the available tributyl phosphate molecules.

With sulphuric acid media, the main factor at low acidities is the fall in the activity of the water, since little sulphuric acid is extracted at these concentrations.¹³ As the extraction of sulphuric acid increases with increasing concentration, the "common ion" effect begins to predominate and so D_{Cr} falls.

Macro-scale Extraction from Mineral Acids.—The aim of these experiments was to establish the formula of the chromium(VI) species extracted from *N* aqueous solutions of hydrochloric, hydrobromic, sulphuric, perchloric, and nitric acid. The organic phase was either pure tributyl phosphate or its solutions in cyclohexane.

With aqueous hydrochloric acid, the extraction by a number of tributyl phosphate solutions was studied; the results given in Tables 1—4 refer to solutions of potassium dichromate in *M*-acid.

TABLE 1.

H^+ , Cr(VI) , and Cl^- removed from *M*-hydrochloric acid on equilibration with 25% tributyl phosphate in cyclohexane.

Total Cr(VI) in initial aqueous phase (mmoles)	0.99	1.57	2.04	2.60	3.06	4.12	5.12	6.17
Cr(VI) lost (mmoles)	0.79	1.02	1.33	1.24	1.33	1.20	1.35	1.44
H^+ lost (mmoles)	1.54	1.92	2.17	2.39	2.52	2.80	2.81	2.81
Cl^- lost (mmoles)	0.77	1.01	1.17	1.27	1.36	1.41	1.45	1.51

TABLE 2.

H^+ , Cr(VI) , and Cl^- removed from *M*-hydrochloric acid on equilibration with 50% tributyl phosphate in cyclohexane.

Total Cr(VI) in initial aqueous phase (mmoles)	0.69	1.36	2.07	2.75	3.40	4.08	4.75	5.46
Cr(VI) lost (mmoles)	0.67	1.32	1.95	2.41	2.64	2.75	2.89	2.94
H^+ lost (mmoles)	1.25	2.48	3.73	4.72	5.05	5.30	5.50	5.60
Cl^- lost (mmoles)	0.82	1.37	1.92	2.48	2.68	2.79	2.87	2.93

TABLE 3.

H^+ , Cr(VI) , and Cl^- removed from *M*-hydrochloric acid on equilibration with 75% tributyl phosphate in cyclohexane.

Total Cr(VI) in initial aqueous phase (mmoles)	0.68	1.45	1.97	2.77	3.37	4.12	4.76	5.40	6.13
Cr(VI) lost (mmoles)	0.68	1.45	1.97	2.72	3.20	3.55	3.70	3.81	3.87
H^+ lost (mmoles)	1.22	2.71	3.96	5.22	6.46	6.97	7.64	7.77	7.77
Cl^- lost (mmoles)	0.87	1.64	1.99	2.65	3.13	3.47	3.61	3.71	3.70

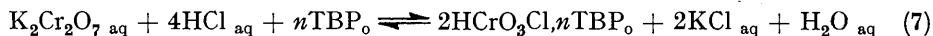
¹⁵ Diamond, *J. Phys. Chem.*, 1957, **61**, 1522.

TABLE 4.

H⁺, Cr(VI), and Cl⁻ removed from M-hydrochloric acid on equilibration with tributyl phosphate.

Total Cr(VI) in initial aqueous phase (mmoles)	1.72	3.87	6.62	9.97	11.30	13.56	14.90	18.80
Cr(VI) lost (mmoles)	1.72	3.87	6.04	6.69	6.94	6.63	6.98	7.03
H ⁺ lost (mmoles)	3.28	7.41	11.73	13.00	13.27	13.50	13.60	13.50
Cl ⁻ lost (mmoles)	1.89	3.82	5.94	6.56	6.51	6.66	6.93	6.96

The interpretation of these results is simplified by the fact that M-hydrochloric acid is only weakly extracted by the organic phase ($D \sim 0.05$ with pure tributyl phosphate, decreasing with its dilution), so that virtually all the hydrogen and chloride ion removed from the aqueous phase is associated with the extraction of chromium(VI). In every case, the ratio H⁺ : Cr(VI) : Cl⁻ removed from the aqueous phase is 2 : 1 : 1, and it follows that the overall extraction process can be represented by



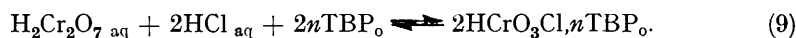
This conclusion was confirmed by extracting solutions prepared by dissolving chromium trioxide in M-hydrochloric acid, and extracting them with 50% tributyl phosphate in cyclohexane. The results are shown in Table 5.

TABLE 5.

H⁺, Cr(VI), and Cl⁻ removed from M-hydrochloric acid solutions of CrO₃ on equilibration with 50% tributyl phosphate in cyclohexane.

Total Cr(VI) in initial aqueous phase (mmoles)	1.37	2.51	3.49	4.89	7.19	12.55
Cr(VI) lost (mmoles)	1.27	2.31	2.91	3.33	3.92	4.55
H ⁺ lost (mmoles)	1.40	2.18	2.72	3.20	3.67	4.10
Cl ⁻ lost (mmoles)	1.11	2.08	2.61	2.92	3.46	4.04

In this case the ratio H⁺ : Cr(VI) : Cl⁻ removed is 1 : 1 : 1, and the simplest overall way of representing the extraction is therefore



Specker and Arend⁷ have also identified chlorochromic acid in tributyl phosphate extracts from hydrochloric acid solution by a spectrophotometric method (see below).

With solutions of potassium dichromate in M-hydrobromic acid, an analogous series of extractions were carried out with tributyl phosphate in cyclohexane.

TABLE 6.

H⁺, Cr(VI), and Br⁻ removed from M-hydrobromic acid solutions of K₂Cr₂O₇ on equilibration with 50% tributyl phosphate in cyclohexane.

Total Cr(VI) in initial aqueous phase (mmoles)	0.67	1.32	2.07	2.67	3.84	4.81	5.71	7.00
Cr(VI) lost (mmoles)	0.67	1.21	1.88	2.33	2.52	2.62	2.64	2.65
H ⁺ lost (mmoles)	1.37	2.45	3.62	4.72	5.09	5.14	5.13	5.01
Br ⁻ lost (mmoles)	0.74	1.25	1.91	2.32	2.50	2.59	2.61	2.67

Inspection of these results shows that the ratio H⁺ : Cr(VI) : Br⁻ lost is 2 : 1 : 1 within experimental error, and we therefore write an equation similar to eqn. (7)



Here again, the interpretation is simplified by the poor extraction of hydrobromic acid by tributyl phosphate under the conditions used.¹³

This relatively weak extraction of the acidifying agent also simplifies the interpretation of results obtained with solutions of potassium dichromate in 0.5M-sulphuric acid. With

an organic phase consisting of 50% tributyl phosphate in cyclohexane no loss of sulphate from the aqueous phase was detected. The results are shown in Table 7.

TABLE 7.

Cr(vi) and H⁺ removed from 0.5M-sulphuric acid containing potassium dichromate on equilibration with 50% tributyl phosphate in cyclohexane.

Total Cr(vi) in initial aqueous phase (mmoles)	1.02	2.08	3.16	4.21	5.16	6.18	7.18
Cr(vi) lost (mmoles)	0.50	0.85	1.09	1.28	1.44	1.57	1.74
H ⁺ lost (mmoles)	0.47	0.84	1.09	1.36	1.58	1.54	1.77

The removal of equimolar quantities of H⁺ and Cr(vi) shows that the extracted species must be H₂Cr₂O₇ and not H₂CrO₄. The same conclusion was reached in the system sodium dichromate-m-perchloric acid-50% tributyl phosphate in cyclohexane. The analysis is here complicated by the comparatively high extraction of perchloric acid, and by the lack of a suitable method for determining perchlorate accurately in the solutions used. It was however possible to show that when only small amounts of chromium(vi) are present in the organic phase, there is a linear relation between the amounts of H⁺ and of Cr(vi) extracted (Fig. 3). The point corresponding to no chromium(vi) extracted is for m-perchloric acid equilibrated with 50% tributyl phosphate. Up to ~0.35 mmole of chromium(vi) extracted the curve is linear, with a slope of 0.93 H⁺ : 1 Cr(vi). Beyond about 0.5 mmole of chromium(vi), the amount of hydrogen ion extracted tends to remain

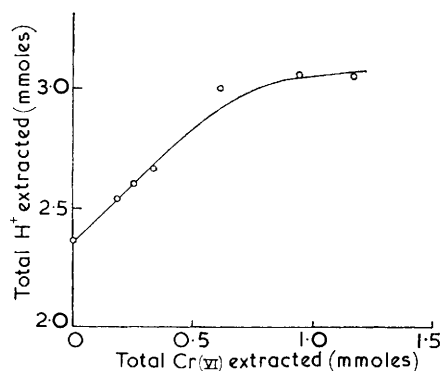


FIG. 3. Extraction of H⁺ and Cr(vi) from solutions of sodium dichromate in m-perchloric acid by 50% tributyl phosphate in cyclohexane.

constant, suggesting that competition is occurring between perchloric acid and dichromic acid for the available tributyl phosphate molecules.

It was not possible to deduce the formula of the species extracted from m-nitric acid by any of the methods used above, since the high extraction of nitric acid relative to chromium(vi), coupled with the lack of a sensitive method for nitrate analysis, rendered the analytical data unreliable. As the amount of chromium(vi) extracted increases, a virtually constant amount of hydrogen ion is removed from the aqueous phase. Identification of the species in the organic phase therefore rests on the spectral data.

Spectrophotometric Results.—The literature data show that Cr₂O₇²⁻, CrO₄²⁻, and CrO₃F⁻ have different absorption spectra which have been used to identify the species in aqueous solution.^{11,12,16} We find that chromium trioxide in dilute sodium hydroxide gives bands at 36,400 and 26,400 cm.⁻¹ and in dilute sulphuric acid at 38,400 and 28,600 cm.⁻¹. The ε values are in the ratio 1 : 1.25 in the alkaline solution (*i.e.*, CrO₄²⁻) and 1.7 : 1 in sulphuric acid (*i.e.*, Cr₂O₇²⁻). These results are in agreement with those of Davies and Prue.¹²

All three organic phases obtained by extraction from sulphuric, perchloric, and nitric acids have strong bands at 35,900 and 28,200 cm.⁻¹, with the absorption at the higher

¹⁶ See Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 284.

energy approximately twice as strong as that at $28,200\text{ cm}^{-1}$. We believe that these results, taken in conjunction with the extraction data presented above, show that the same species is present in all three organic solutions, namely solvated dichromic acid. With organic extracts prepared from hydrochloric or hydrobromic acid, however, we find strong bands at $40,900$ and $35,300$ (HCl) or $36,000\text{ cm}^{-1}$ (HBr), plus a band showing considerable vibrational structure at $28,100$ — $25,800$ (HCl) or $28,700$ — $24,900\text{ cm}^{-1}$ (HBr). The CrO_3F^- anion absorbs at $36,000$ and $28,500\text{ cm}^{-1}$, with the latter band having fine structure.¹⁶ Cohen and Westheimer¹⁷ have identified the chlorochromate ion, CrO_3Cl^- , in 86.5% acetic acid solution, and report strong absorption at $33,100$ and $27,900\text{ cm}^{-1}$.

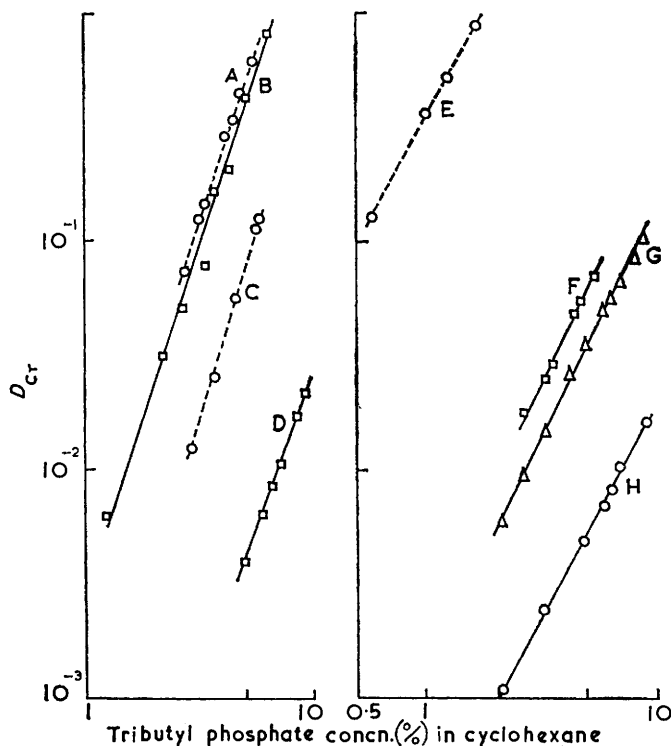


FIG. 4. D_{Cr} as a function of tributyl phosphate concentration in cyclohexane.

A, 3M-HCl; B, 3M-HBr; C, M-HCl; D, M- H_2SO_4 ; E, 8M-HCl; F, 5M- H_2SO_4 ;
G, 3M- HClO_4 ; H, 3M- HNO_3 .

The spectra of the present organic solutions therefore confirm the deduction that the species present are solvated chloro- and bromo-chromic acid, respectively.

The extraction of dichromic rather than chromic acid is in agreement with the discussion given elsewhere¹³ of the effect of anion size on the extraction of acids into basic solvents. The apparently preferential extraction of chlorochromic acid is less easy to explain. There are a number of different possibilities. For instance, chlorochromic acid may be formed in the organic phase from the reaction of $\text{H}_2\text{Cr}_2\text{O}_7 + \text{HCl}_0$, and we have shown by spectral methods that this reaction does indeed occur when two such tributyl phosphate solutions are mixed. Alternatively, the chlorochromate ion may exist in aqueous solutions of chromium(VI) in hydrochloric acid in equilibrium with $\text{Cr}_2\text{O}_7^{2-}$, HCr_2O_7^- etc., and be preferentially extracted. Certainly the absorption spectra of such solutions differ

¹⁷ Cohen and Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4389.

markedly from those in sulphuric acid, which may support the existence of the necessary equilibria. If this theory is correct, one must conclude that the chlorochromate anion is less strongly solvated in the aqueous phase than is dichromate, and is therefore extracted better, and in this respect the very high distribution coefficients reported for the tetrahalogeno-complexes of transition metals¹⁴ may be significant. Further work on this point is being carried out. The same arguments can be applied to bromochromic acid, although in this case the size of the anions CrO_3Br^- and HCr_2O_7^- must be closer than in the chlorochromate case.

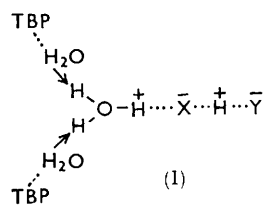
The Solvation Number in the Organic Phase.—It is well established that the number of (say) tributyl phosphate molecules solvating an extracted molecule in the organic phase can be determined by measuring D at different tributyl phosphate concentrations in dilute solutions. The limitations of this method have been discussed by Hesford and McKay,¹⁸ who derive the expression

$$\log D = \text{const} + n \log [\text{TBP}],$$

where D is the distribution coefficient, n the number of tributyl phosphate molecules per extracted molecule, and $[\text{TBP}]$ the concentration of tributyl phosphate in some inert solvent. We have used tracer methods to obtain n for chromium(vi) extracted into tributyl phosphate (1—10%) in cyclohexane from aqueous phases of 1-, 3-, and 8M-hydrochloric acid, 3M-hydrobromic acid, 1- and 5M-sulphuric acid, 3M-perchloric acid, and 3M-nitric acid. In all these experiments the organic phase was pre-equilibrated with the appropriate acid solution before use. In four cases (M- and 3M-hydrochloric, 3M-hydrobromic, and M-sulphuric), the slope was 3.0 ± 0.1 . It has been shown¹⁹ that when very strong acids are extracted by tributyl phosphate, the proton exists in the organic phase as the symmetrical trihydrate of H_3O^+ (*i.e.*, H_9O_4^+). The solvation number of 3 now found for the three acids HCrO_3Cl , HCrO_3Br , and $\text{H}_2\text{Cr}_2\text{O}_7$ therefore arises from the co-ordination of a tributyl phosphate molecule to one of the protons of each of the three "outer" water molecules. Shevchenko *et al.*⁸ found $n = 3$ for extraction from dilute ($< 1\text{M}$) perchloric acid solution. Similar values have also been found for other acid species^{20,21} extracted into basic solvents, and provide additional evidence, with the present results, for the importance of H_9O_4^+ species in solvent extraction.

In the remainder of the systems studied the value of n is significantly less than 3, the actual values being 1.89 in 8M-hydrochloric, 2.13 in 5M-sulphuric, 1.98 in 3M-perchloric, and 1.93 in 3M-nitric acid. These lower solvation numbers are only found when the medium acid itself is comparatively well extracted by the tributyl phosphate solutions, and we therefore take this lowering of n to be the result of competition between the two acids extracted for the available tributyl phosphate. A reduction in n with increasing loading of the organic phase was also found in the extraction of tetrachloroauric acid.²⁰ The fairly good agreement around $n = 2$ may be fortuitous; it seems more likely however that it points to the formation of dipole adducts which can be written as (I). These would only occur at comparatively high concentrations of other acids. A value of 2 for n would be found irrespective of whether X^- or Y^- represents the chromium(vi) anion.

Comparison with Previous Results.—Specker and Arend⁷ reported the identification of $\text{HCrO}_3\text{Cl} \cdot 2\text{TBP}$ in tributyl phosphate equilibrated with hydrochloric acid, but gave no details of concentrations, etc. This result is in agreement with our value of $n = 2$ from 8M-hydrochloric acid. We also confirm their finding that dichromic acid is extracted from



¹⁸ Hesford and McKay, *Trans. Faraday Soc.*, 1958, **54**, 573.

¹⁹ Tuck and Diamond, *J. Phys. Chem.*, 1961, **65**, 193.

²⁰ Diamond and Tuck, UCRL-8897.

²¹ Tuck, *J. Inorg. Nuclear Chem.*, 1959, **11**, 164; Casey and Maddock, *Trans. Faraday Soc.*, 1962, **58**, 918; Diamond, personal communication.

aqueous sulphuric acid. White and Ross⁶ claimed to have extracted this species into solutions of trioctylphosphine oxide from aqueous hydrochloric acid solutions of dichromate; we believe that their results can be re-interpreted in terms of solvated chlorochromic acid in the organic phase.

As noted earlier, Shevchenko *et al.* found a tributyl phosphate solvation number of 3 from dilute aqueous perchloric acid, and assumed that this value holds at all concentrations of chromium and of acid. In fact, as shown above, $n = 2$ in the 3M-nitric acid used in some of their experiments. Treatment of the various equilibria involved on the assumption that $n = 3$ leads them to the conclusion that the species in the organic phase is H_2CrO_4 . This does not agree with our findings, and we believe that changes in n with concentration must necessarily vitiate their mathematical treatment, and hence their conclusions.

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