901. *The Degradation of Tri-n-butyl Phosphate by Chromium*(VI).

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The products of the decomposition of extract solutions of chromium(VI) in tri-n-butyl phosphate are chromium(III), butanol, butyraldehyde, butyric acid, and dibutyl hydrogen phosphate. The nature of the chromium(III) species has been investigated. The rates of reaction in perchloric, sulphuric, hydrochloric, and nitric acid media are shown to agree with published views on the mechanism of the chromium(VI) oxidation of organic molecules.

One reason for the widespread use of tri-n-butyl phosphate in solvent extractions is the resistance of this solvent to both hydrolysis and oxidation. There has, however, been some interest in the rates at which these processes do occur, and in the degradation products which result; in particular, recent work has been concerned with the irreversible acid-catalysed hydrolysis which occurs when the solvent is in contact with mineral acids. Burger [1] has reviewed data on the hydrolysis by nitric acid, which is of particular interest because many industrial methods of separation in the nuclear-energy field involve aqueous nitric acid. Hydrolysis by hydrochloric acid has been studied by Kennedy and Grimley,[2] and by Kertes and Halpern.[3]

There is less information available on the stability of this solvent towards oxidising agents, although in one of the first reports of its use in extracting metal complexes,[4] the resistance to oxidation by cerium(IV) was noted. In the course of an investigation into the nature of the chromium(VI) species extracted into tri-n-butyl phosphate from various aqueous mineral acids,[5] it was found that reduction to chromium(III) occurred in the organic phase at rates which depended on the acid used. We have now measured the rates of these processes quantitatively, and have investigated the nature of both the organic and inorganic products of reaction. The work has been confined to pure (*i.e.*, undiluted) tri-n-butyl phosphate, and to degradation in the organic phase only, any reactions in the aqueous phase being neglected.

EXPERIMENTAL

Materials.—All reagents were as described earlier.[5]

Identification of Chromium(III) *Species.*—Suitable quantities of chromium trioxide were dissolved in N-aqueous solutions of nitric, perchloric, sulphuric, hydrochloric, or hydrobromic acid, equilibrated with an equal volume of tri-n-butyl phosphate, and the organic phase separated by centrifugation. These organic solutions were then kept at room temperature until the characteristic orange colour of the chromium(VI) species [5] had disappeared. The absorption spectra of these organic solutions, and of the aqueous solutions obtained on back-washing with water, were measured with a Unicam S.P. 500 spectrophotometer.

Kinetic Studies.—The rates of reduction of chromium(VI) in extract tri-n-butyl phosphate solutions prepared from aqueous perchloric, sulphuric, nitric, and hydrochloric acid media were followed spectrophotometrically in a Unicam S.P. 500 spectrophotometer fitted with a thermostatically controlled cell-holder. All measurements were carried out at 25° ± 0·2°. In a typical experiment, 3 ml. of a standard [0·006M in Cr(VI)] solution of chromium trioxide in M-perchloric acid was equilibrated with 3 ml. of tri-n-butyl phosphate, and the separated organic phase placed in a thermostat at 25°. A solution (of known strength) of perchloric acid in tri-n-butyl phosphate was prepared in a similar manner. These solutions were then mixed in the spectrophotometer cell, and the intensity of the 360 mμ absorption [corresponding to Cr(VI)] measured as a function of time. With acids other than perchloric, it was necessary to

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[1] Burger in "Progress in Nuclear Energy," Series III, "Process Chemistry," Vol. 2, Pergamon Press, London, 1958, p. 307.

[2] Kennedy and Grimley, U.K. Atomic Energy Authority, report AERE C/R 1284.

[3] Kertes and Halpern, *J. Inorg. Nuclear Chem.*, 1961, **20**, 117.

[4] Warf, *J. Amer. Chem. Soc.*, 1949, **71**, 3257.

[5] Tuck and Walters, *J.*, 1963, 1111.

run the mixed solutions through a sintered-glass disc to remove the cloudiness which appeared in mixing, probably due to water being thrown out of solution. In no case did the extraction, mixing, and filtration procedure require more than 7—8 min., which was short compared with the period over which the kinetics were followed (of the order of 10—100 hr.).

Corrections were not necessary for the negligible optical density of the chromium(III) species at the wavelengths used. The concentration of acid in the mixture was determined by titration in neutralised aqueous acetone; any errors due to the oxidation of the acetone by unchanged chromium(VI) (initial concn. 0·006M) were ignored.

Identification of Organic Products of Degradation.—A tri-n-butyl phosphate solution, 0·06M in chromium(VI), was prepared by extraction from 2M-perchloric acid. After centrifugation, the separated organic phase was left at room temperature for some hours and finally heated on a water bath to ensure complete reduction of the chromium(VI). The resultant blue solution was distilled in a vacuum at 90°, volatile products being collected in a trap at −190°. Analysis of this fraction by gas–liquid chromatography (g.l.c.) in a Perkin-Elmer "Fraktometer" (2 m. column of 1% silicone elastomer E301, supported on glass beads; column temp. 70°; nitrogen carrier gas) showed only four organic compounds to be present; these were identified by comparing the measured retention times with those of known compounds.

RESULTS AND DISCUSSION

Products of Reduction of Chromium(VI).—Previous work [5] has shown that the species extracted into tri-n-butyl phosphate solution are: (solvated) $H_2Cr_2O_7$ from nitric, perchloric, and sulphuric acid media; $HCrO_3Cl$ from hydrochloric acid; and $HCrO_3Br$ from hydrobromic acid solution. Each acid system behaved differently in the present study. It should be emphasised that the amount of "medium" acid extracted into tri-n-butyl phosphate, from solutions initially N in acid, decreases [6] in the order $HNO_3 \approx HClO_4 > HBr > HCl > H_2SO_4$, and that some of the qualitative differences found may result from widely differing concentrations of acid in the organic phase.

Reduction of chromium(VI) by tri-n-butyl phosphate containing nitric acid gave a green organic phase, stable for several weeks. Back-washing with water gave a green aqueous phase which quickly (*ca.* 1 hr.) became blue; the absorption spectrum ($\lambda_{max.}$ 407 and 571 mμ) showed that this blue species was $[Cr(H_2O)_6]^{3+}$ (*cf.* $\lambda_{max.}$ 407 and 575 mμ reported by Elving and Zemel [7]). The green species initially present in the aqueous backwash solution was not identified. When a chromium(VI) solution in tri-n-butyl phosphate which had been kept for about 18 months was heated gently, the solution became turbid. Further heating caused this turbidity to disappear, but on cooling, a green gelatinous precipitate was formed. This was centrifuged out, washed several times with acetone, dried, and analysed (Found: C, 47·0%; H, 8·3%; Cr, 5·2%). The formulation of this material is difficult in the absence of structural information, but the C : H ratio suggests the presence of n-butyl groups; probably tri-, di-, or mono-n-butyl phosphate residues are co-ordinated to a polymeric $[O\text{–}Cr^{III}\text{–}O]_n$ framework. The analytical data rule out any simple chromium(III)–di-n-butyl phosphate compound. It is worth reporting in this connection that, although Burger [1] quotes results on the extraction of chromium by di-n-butyl phosphate, neither with $[Cr(H_2O)_6]^{3+}$ in neutral solution or dilute perchloric acid, nor with $[Cr(H_2O)_5Cl]^{2+}$, in neutral solution or dilute hydrochloric acid, was there any evidence of extraction into solutions of di-n-butyl phosphate in cyclohexane.

A solution of chromium(VI) in perchloric acid gave rise to a blue organic phase, stable for some months; back-washing with water gave an aqueous solution of chromium(III) hexahydrate. Tri-n-butyl phosphate solutions, prepared from sulphuric acid, spontaneously precipitated droplets of a blue aqueous phase, leaving a colourless organic solution; this aqueous phase was again found to contain $[Cr(H_2O)_6]^{3+}$ ($\lambda_{max.}$ 410 and 580 mμ). The peculiar behaviour of the sulphuric acid system may be related to the low concentration of acid in the organic phase.[6]

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[6] Tuck, *J.*, 1963, 2736.

[7] Elving and Zemel, *J. Amer. Chem. Soc.*, 1957, **79**, 1281.

Degradation of tri-n-butyl phosphate solutions containing chlorochromic acid produced a stable green organic phase. The green aqueous solution produced on back-washing this phase with water was shown to contain $[Cr(H_2O)_5Cl]^{2+}$ ($\lambda_{max.}$ 425 and 598 mμ; *cf.* 430 and 605 reported earlier [7]), so that the Cr–Cl bond, present in the extracted chromium(VI) species, obviously persists throughout the reduction process. After about 2 months, the green aqueous solution became blue, owing to hydrolysis of $[Cr(H_2O)_5Cl]^{2+}$ to the hexahydrate.[7] Similar results were obtained with bromochromic acid. The green aqueous back-wash solution had $\lambda_{max.}$ 415 and 575 mμ and, although there are no data in the literature for the absorption spectrum of $[Cr(H_2O)_5Br]^{2+}$, we feel confident that this is the species initially present. Hydrolysis to the blue chromium(III) hexahydrate is again complete in about 2 months. It should be noted that extraction of chromium(VI) from the appropriate aqueous solution, followed by reduction and back-washing, may in some cases be a useful way of obtaining aqueous solutions of $[Cr(H_2O)_5X]$ species.

Products of Degradation of Tri-n-butyl Phosphate.—G.l.c. analysis showed that the four main products of the degradation were butyraldehyde (retention time, 24 sec.), butanol (54 sec.), dibutyl phosphate (2·96 min.), and butyric acid (6·42 min.). The retention times were sufficiently different to allow easy identification of these products; it was not possible to make any estimate of the relative amounts present.

Kinetics and Mechanism of Reaction.—The decrease in the optical density of the chromium(VI) absorption followed first-order kinetics; the rate-constants, evaluated graphically from the experimental results, were as defined by

$$-d[Cr^{VI}]/dt = k[Cr^{VI}]$$

The dependence of k on the concentration of extracted acid in the tri-n-butyl phosphate solution is shown in the Table. For perchloric, sulphuric, and hydrochloric acid, k increases with increasing acid concentration; for nitric acid, the reverse is the case.

Rate constants for reduction of chromium(VI) in tri-n-butyl phosphate as a function of the concentration of extracted acid.

Perchloric acid: concn. (M)	0·35	0·51	0·59	0·66	0·81	0·88	0·93	1·05	1·16
10^4k (sec.$^{-1}$)	0·30	0·86	1·45	2·39	4·73	6·28	9·00	15·5	25·4
Sulphuric acid: concn. (M)	0·14	0·20	0·34	0·47	0·64	0·83			
10^5k (sec.$^{-1}$)	1·47	1·79	2·39	3·03	3·41	4·28			
Nitric acid: concn. (M)	0·18	0·39	0·51	0·70	0·95	0·97	1·23		
10^6k (sec.$^{-1}$)	19·4	11·2	8·67	6·67	5·45	5·39	4·91		
Hydrochloric acid: concn. (M)	0·27	0·47	0·71	0·92	1·22	1·47	1·64		
10^6k (sec.$^{-1}$)	1·62	1·79	2·42	3·47	5·46	7·73	9·37		

We can immediately rule out any scheme for the mechanism of the reaction which involves acid hydrolysis of tri-n-butyl phosphate as a preliminary step to oxidation

$$(Bu^nO)_3P{\rightarrow}O \xrightarrow{H^+ \text{ catalysis}} HO(Bu^nO)_2P{\rightarrow}O \qquad (1)$$

because this would give rates of reaction appreciably lower than those actually observed. Thus for 0·86M-nitric acid in tri-n-butyl phosphate at 30°, the rate of hydrolysis (= rate of formation of n-butanol) is $1·4 \times 10^{-9}$ mole sec.$^{-1}$ (data from Burger [1]) which is some 30 times lower than the (interpolated) rate of 4×10^{-8} mole sec.$^{-1}$ for $d[Cr^{VI}]/dt$ at 25°. Similar arguments, using the results of Kertes and Halpern,[3] rule out hydrolysis in the case of hydrochloric acid solutions. Furthermore, it is difficult to see why such a mechanism should yield a first-order dependence on concentration of chromium(VI).

We suggest that in perchloric and sulphuric acid media, in which the chromium(VI) species is solvated $H_2Cr_2O_7$,[5] the results can be explained in terms of a mechanism similar to that suggested for the oxidation by chromium(VI) of alcohols.[8] The simplest reaction scheme involves $H_2Cr_2O_7$ species only, although, of course, decomposition *via* H_2CrO_4 and its derivatives cannot be excluded. Writing the solvated $H_9O_4^+$ cation [9] as $(BuO)_3PO{\cdot}H^+$ one has:

(*a*) trans-esterification

$$H_2Cr_2O_7 + (Bu^nO)_3PO{\cdot}H^+ \underset{\text{equilibration}}{\overset{\text{rapid}}{\rightleftharpoons}} HO{\cdot}CrO_2{\cdot}O{\cdot}CrO_2{\cdot}OBu^n + (Bu^nO)_2P(OH)_2^+ \qquad (2)$$

(*b*) ester decomposition

$$HO{\cdot}CrO_2{\cdot}O{\cdot}CrO_2{\cdot}OBu^n \xrightarrow[\text{rate-controlling}]{\text{slow decomposition}} Cr^{III} + \text{oxidation products} \qquad (3$$

This scheme explains the dependence of the rate on acid concentration, the acid being able to catalyse both (2) and (3), and also the first-order disappearance of chromium(VI) species. The present work casts no light on the mechanism of the suggested rate-controlling process (3); the analogous decomposition of n-butyl chromate and similar compounds is discussed by Waters.[8] The above scheme also explains why the rate is higher in perchloric acid media than in sulphuric acid, since the former acid is the stronger in tri-n-butyl phosphate.[10] A similar mechanism can be written for hydrochloric acid solutions, in which the chromium(VI) species is solvated chlorochromic acid. At a given acidity, the rate is lower than in the other acids studied, in agreement with earlier findings [8] that chlorochromic acid is a less efficient oxidising agent than the completely oxygenated anionic species.

Solutions of nitric acid in tri-n-butyl phosphate (TBP) are different in that the acid species is here TBP,HNO_3 rather than TBP,$H_9O_4^+X^-$, so that rates of reactions involving acid catalysis cannot be directly compared with those discussed above. The rate, in fact, decreases with increasing concentration of nitric acid. It is known, however, that the decomposition of di-isopropyl chromate is catalysed by base (pyridine).[8,11] It has been shown previously [12,13] that the water content of solutions of nitric acid in tri-n-butyl phosphate decreases with increasing concentration of acid, and we therefore suggest that the apparent inverse dependence of rate on acid concentration reflects, in fact, catalysis of process (3) by TBP,H_2O.

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[9] Tuck and Diamond, *J. Phys. Chem.*, 1961, **65**, 193.
[10] Hesford and McKay, *J. Inorg. Nuclear Chem.*, 1960, **13**, 156.
[11] Leo and Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4383.
[12] Alcock, Grimley, Healy, Kennedy, and McKay, *Trans. Faraday Soc.*, 1956, **52**, 39.
[13] Tuck, *J.*, 1958, 2783.