644. *The Rate of Formation of Perchromic Acid in a Non-aqueous Medium.*

By D. G. Tuck and R. M. Walters.

The formation of perchromic acid from chromium(VI) and hydrogen peroxide is very rapid in aqueous solution, but can be studied kinetically in tri-n-butyl phosphate–cyclohexane mixtures, in which the product is fairly stable. Spectrophotometry shows that the reaction is of first order in both chromium(VI) and hydrogen peroxide, and is acid-catalysed. The mechanism is discussed.

THE reaction between chromium(VI) and hydrogen peroxide in acidic aqueous solution gives the well-known blue perchromic acid, the formula [1] of which is now established as CrO_5 (but see ref. 2 for a discussion of the inadequacy of this). In aqueous solution, perchromic acid is highly reactive, decomposing so quickly as to make the measurement of its formation constant experimentally difficult,[1c] so it has not so far been possible to study the kinetics of formation in aqueous solution. Both chromium(VI) [3] and hydrogen peroxide [4] can, however, be extracted into basic organic solvents; in particular, the species present in extract solutions in tri-n-butyl phosphate (TBP) have been identified.[3,4] The nature of the chromium(VI) species extracted from aqueous acidic solution depends on the acid present, being (solvated) $H_2Cr_2O_7$ in the presence of nitric, perchloric, and sulphuric acid, and $HCrO_3X$ (X = Cl, Br) with hydrochloric or hydrobromic acid. The extraction of hydrogen peroxide involves replacement of TBP,H_2O by TBP,H_2O_2 in the organic phase. The reaction between chromium(VI) and hydrogen peroxide in tributyl phosphate produces perchromic acid, which is stable for many days at chromium(VI) concentrations of $10^{-3}M$ and below. Perchromic acid itself can be extracted from aqueous solution by basic solvents,[1c] a property which has useful analytical applications.[5]

By adjusting the concentrations of chromium(V) and hydrogen peroxide, the rate of formation of perchromic acid in tributyl phosphate can be made sufficiently low to allow the kinetics to be studied. Extract solutions in pure (*i.e.*, undiluted) tributyl phosphate were not in fact used, since mixing such solutions did not give a clear transparent phase suitable for spectrophotometry. This complication, probably caused by precipitation of droplets of water, was avoided by using 50% (v/v) solutions of tributyl phosphate in cyclohexane as the organic phase in all experiments. This had the further advantage of

[1] (a) Glasner, *J.*, 1950, 2795; (b) Glasner and Steinberg, *J.*, 1957, 2569; (c) Evans, *J.*, 1957, 4013.
[2] Tuck and Walters, *Inorg. Chem.*, 1963, **2**, 428.
[3] Tuck and Walters, *J.*, 1963, 1111, and refs. therein.
[4] Tuck, *J.*, 1959, 218, and refs. therein.
[5] (a) Brookshier and Freund, *Analyt. Chem.*, 1951, **23**, 110; (b) Glasner and Steinberg, *ibid.*, 1955, **27**, 2008; (c) Tuck, *Analyt. Chim. Acta*, 1962, **27**, 296; (d) Sastri and Sundar, *Z. analyt. Chem.*, 1963, **193**, 343.

reducing the rate of reaction. Preliminary studies showed that the reaction is acid-catalysed, and chromium(VI) extract solutions were consequently prepared from dilute sulphuric acid aqueous solutions, since this acid is only weakly extracted into tributyl phosphate from dilute solution.[6]

EXPERIMENTAL

Materials.—Organic solvents were as in previous work;[3] solutions of dry TBP in cyclohexane were prepared immediately prior to use.

A chromium(VI) stock aqueous solution was prepared by dissolving 25 mg. of AnalaR chromium trioxide in 50 ml. of 0·25M-sulphuric acid.

Hydrogen peroxide (B.D.H., analytical reagent grade, 100 volume) was diluted tenfold to give a stock solution 0·887M (permanganate titration); equilibration with 50% tributyl phosphate–cyclohexane gave an organic phase 0·124M in hydrogen peroxide.

Spectrophotometry.—All measurements were made in a Unicam S.P. 500 instrument; 4-cm. glass cells (capacity 12 ml.) were held in a thermostated cell-holder at 25·0 ± 0·2°. In the kinetic studies (see below) one reactant solution was normally placed in the cell for ~30 min., and the other held in a 25° thermostat for a similar period before mixing.

Initial experiments involved the measurement of the molar extinction coefficient for chromium(VI) as $H_2Cr_2O_7$ in 50% tributyl phosphate–cyclohexane at 360 and 575 mμ. An aliquot portion of the stock aqueous solution was equilibrated with the organic medium, and the absorbance of the equilibrium phase measured after suitable dilution. The chromium(VI) removed from the aqueous phase (and hence the concentration in the equilibrium organic phase) was determined by thiosulphate titration. The mean of three such experiments gave $\varepsilon = 1\cdot727 \times 10^3$ at 360 mμ, and ε ~20 at 575 mμ. The uncertainty in the latter value is negligible, since perchromic acid has a high ε at this wavelength.

In order to measure ε for perchromic acid, an extract of chromium(VI) solution of known concentration was mixed with extract solutions of perchloric acid and hydrogen peroxide in 50% tributyl phosphate–cyclohexane. The approximate concentrations in the solution whose absorbance was measured were Cr^{VI} 10^{-3}M, perchloric acid and hydrogen peroxide each 10^{-2}M. Evans[1c] has shown that the formation constant for perchromic acid under the aqueous conditions studied by him is very high, and so we assume that in the presence of excess of acid and hydrogen peroxide, the chromium(VI) in the above solution is present virtually completely as perchromic acid. The molar extinction coefficients are then $\varepsilon_{360} = 212$ and $\varepsilon_{575} = 878$ (mean of three experiments). Repetition of the measurements at higher acid and hydrogen peroxide concentrations gave 214 and 875, showing the assumption of complete conversion into perchromic acid to be substantially correct.

Rate Measurements.—The absorbance of the reaction mixture was measured as described by Evans.[1c] A cell containing 50% tributyl phosphate–cyclohexane was placed in the light beam and the slit width adjusted to give a zero reading on the meter; the slit width was held constant throughout an experiment. The cell containing the chromium(VI) solution was then placed in the light beam, the hydrogen peroxide added as quickly as possible, with stirring, from a syringe, and the lid of the cell replaced. The dark current shutter was opened, and the absorbance measurement made by setting the absorbance dial at some pre-determined value and noting the time at which the meter needle returned to zero.

The velocity constant was most easily determined by following the rate of formation of perchromic acid, $+[CrO_5]/dt$, from absorbance measurements at 575 mμ. The experimental concentrations of chromium(VI) and hydrogen peroxide ensured that although there was an initial (molar) excess of hydrogen peroxide, this was insufficient for complete conversion of chromium(VI) into perchromic acid (see discussion of the stoicheiometry). Corrections were made for the absorbance by unchanged chromium(VI).

With the concentrations and time intervals used, effects due to degradation of the solvent[7] by chromium(VI) were negligible.

Order of Reaction.—The change in absorbance at 360 mμ can be expressed as

$$-\mathrm{d}[Cr^{VI}]/\mathrm{d}t = k[Cr^{VI}]_{n1}[H_2O_2]_{n2}[H^+]_{n3}$$

[6] Tuck, *J.*, 1963, 2736.
[7] Tuck and Walters, *J.*, 1963, 4712.

where Cr^{IV} implies solvated $H_2Cr_2O_7$ and the n's are the respective reaction orders: $[H^+]$ is the total acid concentration (*i.e.*, $H_2Cr_2O_7$ plus co-extracted acid), though not of course present as free hydrogen ions. By arranging for two of the species involved to be in excess of the third, the order of reaction with respect to the third reactant was found. To determine the order for chromium(VI) the experimental method was essentially that described above. Absorbances were plotted against time, and the initial rate of decomposition $-d[Cr^{VI}]/dt$ evaluated fom the slope up to $t = 5$ sec. ·

In the case of hydrogen peroxide, solutions in the concentration range required could not be prepared conveniently by volume dilution; suitable quantities were therefore diluted by weight, and concentrations expressed as molalities. In these experiments, $-d[Cr^{VI}]/dt$ was obtained from the slope over 0—20 sec.

No correction was made for the absorbance of perchromic acid at 360 mμ, but since only the initial part of the reaction was of interest, errors from this source should not be large.

RESULTS AND DISCUSSION

Order of Reaction.—The order with respect to chromium(VI) was measured for chromium(VI) concentrations 4—12 $\times$ 10^{-5}M, with hydrogen peroxide and acid concentrations maintained at 10^{-3}M. Suitable amounts of an extract solution of perchloric acid in 50% TBP–cyclohexane were added for this purpose. The results (Table 1) show that the rate is linear with initial Cr(VI) concentration within experimental error.

TABLE 1.

Initial rate of reaction as a function of initial chromium(VI) concentration.

| Initial $[H_2Cr_2O_7]$ (10^{-5}M)	$-d[Cr^{VI}]/dt$ (10^{-6} mole l.$^{-1}$ sec.$^{-1}$)	Rate/initial concn. (10^{-2} sec.$^{-1}$)
4·35	1·31	3·02
5·81	1·80	3·09
7·24	2·41	3·33
8·70	2·55	2·94
10·2	3·21	3·14
11·6	3·49	3·01
		mean 3·09 $\pm$ 0·04 (σ)

In corresponding experiments to determine the order with respect to hydrogen peroxide, the initial chromium(VI) concentration was 2·17 $\times$ 10^{-4}M. The total acid concentration was not measured; since chromium(VI) is itself present as $H_2Cr_2O_7$, however, and some sulphuric acid is co-extracted,[3] the acid concentration was higher than that of chromium(VI). In calculating the molal hydrogen peroxide in the reaction mixture, the millimolar amounts of other solutes in the solution were ignored. A molal solution corresponds roughly to 0·85M, so that the initial hydrogen peroxide is well below that of both chromium(VI) and acid. Table 2 shows that under the conditions studied, the reaction is of first order in hydrogen peroxide.

TABLE 2.

Initial rate of reaction as a function of initial hydrogen peroxide concentration.

Initial $[H_2O_2]$ (10^{-5} molal)	$-d[Cr^{VI}]/dt$ (10^{-7} mole kg.$^{-1}$ sec.$^{-1}$)	mean 3·09 $\pm$ 0·04 (σ) Rate/initial concn (10^{-2} sec.$^{-1}$)
0·895	5·44	6·08
1·22	7·60	6·23
1·55	9·10	5·86
1·87	11·3	6·05
2·16	12·7	5·88
		mean 6·02 $\pm$ 0·05 (σ)

The order with respect to acid concentration could not be investigated by the method described, since acid concentrations below the chromium(VI) concentration could not be obtained for the reasons discussed above.

Rate-constant Measurements.—Since the species present in the non-aqueous phase has been identified [3] as $H_2Cr_2O_7$ (or $H^+ \cdot HCr_2O_7^-$), the simplest stoicheiometric equation for the formation of perchromic acid is

$$H_2Cr_2O_7 + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O \qquad (2)$$
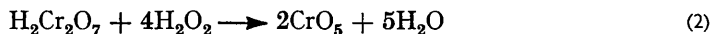
For initial concentrations of a moles per litre of $H_2Cr_2O_7$ and b moles per litre of H_2O_2 giving $2x$ moles per litre of CrO_5 after t sec., the rate equation is

$$+\mathrm{d}[CrO_5]\mathrm{d}t = k(a - x)(b - 4x) \qquad (3)$$

where k is the second-order velocity constant. Integration of (3) gives

$$\frac{1}{4a - b} \ln \frac{b(a - x)}{a(b - 4x)} = kt \qquad (4)$$

The formation of perchromic acid was followed spectrophotometrically on a solution for which $a = 0.179$ and $b = 0.250$mM. The experimental results (Table 3) show good agreement in the values of k calculated from eqn. (4). Since the main interest was in the order of magnitude of the rate constant, rather than in the absolute value, no further experiments of this type were performed.

As noted earlier, the rate of formation of perchromic acid appears to be strongly acid-catalysed. We were unable to study this effect quantitatively because significant increases in acidity above those used gave rates too high for our measuring technique. The different values of k which follow from Tables 1, 2 and 3 (30, 300, and 51, respectively)
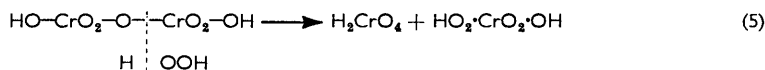
TABLE 3.

Rate of formation of perchromic acid.

Time (sec.)	Absorbance	kt (from eqn. 4) $(10^3 \text{ l. mole}^{-1})$	k (l. mole^{-1} sec.$^{-1}$)
13·3	0·163	0·68	51·1
24·0	0·238	1·21	50·5
33·5	0·292	1·77	52·9
44·0	0·322	2·18	49·6
55·5	0·354	2·79	50·3
80·0	0·393	4·01	50·1
110·0	0·414	5·26	47·8
131·0	0·428	6·95	53·1
		mean 50·7 $\pm$ 0·5 (σ)	

are believed to be the result of catalysis by (*a*) different acids (perchloric and sulphuric in Table 1, sulphuric in Tables 2 and 3), and (*b*) different concentrations of acid due to the slightly different methods of preparing the solutions in each of the three cases.

Reaction Mechanism.—We have discussed [2] the structure of perchromic acid; recent X-ray structural determinations on the pyridine adduct $CrO_5,$py by Stomberg [8] and by Pedersen and Pedersen [9] agree with the postulate of O_2^{2-} groups acting as ligands by donation from the π-orbitals. This type of bonding is assumed in the following discussion.

The first step in the reaction studied is believed to be the fission of the $H_2Cr_2O_7$ molecule by attack by hydrogen peroxide at the Cr–O–Cr link; solvation being ignored, this can be written as

$$\text{HO–CrO}_2\text{–O–}\vert\text{–CrO}_2\text{–OH} \longrightarrow H_2CrO_4 + HO_2 \cdot CrO_2 \cdot OH \qquad (5)$$
$$\text{H} \vert \text{OOH}$$

This is identified as the (fast) rate-controlling process, being of first order in both reactants, and is probably acid-catalysed. Structural evidence on the dichromate anion agrees with

[8] Stomberg, *Nature*, 1962, **196**, 570.
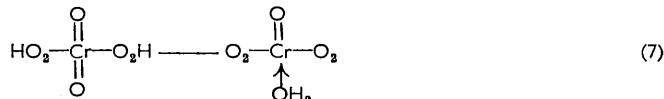[9] Pedersen and Pedersen, *Acta Chem. Scand.*, 1963, **17**, 557.

the postulate of reaction at this link.   The six outer Cr–O bonds are 1·6 Å long,[10] whereas the Cr–O–Cr distances are 1·9 Å; this, plus the non-linearity of these three atoms (Cr–O–Cr angle 115°), suggests that this is a σ-bonded system, whereas the other Cr–O bonds have additional π-character.   A further point is that the reaction of hydrogen peroxide and chromium(VI) in aqueous solution only occurs in the presence of acid, so that in alkaline solution the CrO_4^{2-} ion (Cr–O distance [10] 1·6 Å) resists attack.

The monoperoxy-species produced in reaction (5) can then react with a second molecule of hydrogen peroxide, effectively exchanging OH for O_2H

$$HO_2 \cdot CrO_2 \cdot OH + H_2O_2 \longrightarrow HO_2 \cdot CrO_2 \cdot O_2H + H_2O \qquad (6)$$

followed by an internal rearrangement

$$\underset{\displaystyle \overset{\displaystyle O}{\|}}{HO_2-\overset{\displaystyle O}{\underset{\displaystyle \|}{Cr}}-O_2H} \longrightarrow \underset{\displaystyle \overset{\displaystyle \uparrow}{OH_2}}{O_2-\overset{\displaystyle O}{\underset{\displaystyle \|}{Cr}}-O_2} \qquad (7)$$

Reaction (6) cannot be rate-controlling, since it does not involve first-order dependence on the concentration of $H_2Cr_2O_7$, and also because it would give a dependence on $[H_2O_2]^2$. Reaction (7) would probably be very rapid.

The species CrO_5,H_2O may then simply exchange H_2O for a molecule of tri-butyl phosphate (TBP), to give

$$\underset{\displaystyle \underset{\displaystyle (BuO)_3PO}{\overset{\displaystyle \uparrow}{}}}{O_2-\overset{\displaystyle O}{\underset{\displaystyle \|}{Cr}}-O_2} \qquad (I)$$

or add on a TBP molecule to the already co-ordinated water molecule.   The solvation by TBP may be higher than shown in (1), since Sastri and Sundar [5d] found that the distribution coefficient for the extraction of perchromic acid into dilute solutions of TBP in benzene depends on $[TBP]^2$, implying a disolvate in the organic phase.

We have assumed in the above discussion that the reaction involves neutral molecules only.   The reduction in the rate of reaction on going from pure TBP to TBP–cyclohexane, observed qualitatively, suggests that ion-pairs may be involved.   Since ln k has a dependence on $1/\varepsilon$, a simple extrapolation from $\varepsilon \sim 5$ for 50% TBP–cyclohexane to $\varepsilon = 80$ for water requires a 16-fold increase in ln k.   The exact implications of this are of course questionable, since the reacting species in aqueous solution may not be $Cr_2O_7^{2-}$ [cf. eqn. (5)], but $HCrO_4^-$ (cf. ref. 1c);   the calculation does, however, make clear why the kinetics of this reaction cannot be studied in aqueous solution by normal chemical methods.

[10] Wells, " Structural Inorganic Chemistry," Oxford University Press, 3rd edn., 1962, p. 443.