The Kinetics of the Oxidation of Chromium(II), Titanium(III), and Vanadium(IV) by Hydrogen Peroxide and Hydroxyl Radicals

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The reaction rate constants of $M^{n+} + H_2O_2$ were measured for $M^{n+} = Cr^{II}, Ti^{III}$, and V^{IV}, using the stopped-flow technique, in perchloric and sulphuric acid media. These rate constants, for T^{III} and V^{IV} were found to increase on increasing the pH in the range 0—2·5. The rate constants for the reaction of these metal ions with OH radicals were measured through competition with thiocyanate anions, using the pulse radiolysis technique. It was found that $k_{M^{n+}+OH} = (1{\cdot}2 \pm 0{\cdot}2) \times 10^{10}$, $(3{\cdot}0 \pm 0{\cdot}3) \times 10^{9}$, and $(6{\cdot}4 \pm 0{\cdot}4) \times 10^{8} M^{-1} s^{-1}$ for Cr^{II}, Ti^{III}, and V^{IV} respectively.

THE reaction of H_2O_2 with Ti^{III}, as well as with Fe^{II}, has been widely used as a device for the generation of organic free radicals in aqueous media.[1-3] This was done by mixing H_2O_2, M^{n+},† and an organic substrate in a flow system. The organic radical produced in that reaction mixture was observed later at the observation point. E.s.r. spectra of these organic radicals have been interpreted and the radicals identified, although the chemical character of the primary species and the primary reaction mechanisms are still controversial.[3-5]

Kinetic studies of the $Fe^{II} + H_2O_2$ reaction have been already carried out spectrophotometrically, using the stopped-flow technique,[6-8] but the reaction of Ti^{III} with H_2O_2 has never been thoroughly investigated, in spite of the widespread use of this system as a source for generating various radicals.

The rate of this reaction and its pH dependence is of major importance in applying this reaction in the e.s.r. flow studies. Any kinetic study of radicals thus generated and the related interpretation of the reaction mechanism depends on the knowledge of the rate of the initiating reaction. Numerous erroneous interpretations and kinetic results found in the literature have been caused by the absence of this knowledge.

At least two general mechanisms for the decomposition of H_2O_2 by metal ions have been considered.[9] The reduction might take place *via* either of two successive one-electron stages:

$$M^{n+} + H_2O_2 \xrightarrow{k_1} M^{(n+1)+} + OH^- + OH \quad (1)$$

$$M^{n+} + OH \xrightarrow{k_2} M^{(n+1)+} + OH^- \quad (2)$$

thus yielding free radicals (capable of reacting with various substrates in the reaction mixture), or: through a two-electron single step, according to:

$$M^{n+} + H_2O_2 \longrightarrow M^{(n+2)+} + 2OH^- \quad (3)$$

$$M^{n+} + M^{(n+2)+} \longrightarrow 2M^{(n+1)+} \quad (4)$$

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† The notation M^{n+} represents the metal ion, irrespective of its hydrolysed or complexed form.

[1] W. T. Dixon and R. O. C. Norman, *Nature*, 1962, **196**, 891; R. O. C. Norman and B. L. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[2] R. E. Florin, F. Sicillio, and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 1968, **72*A***, 49.

[3] T. Shiga, *J. Phys. Chem.*, 1965, **69**, 3905.

[4] R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389.

[5] R. E. James and F. Sicillio, *J. Phys. Chem.*, 1970, **74**, 1166.

[6] C. F. Wells and M. A. Salam, *J. Chem. Soc.* (*A*), 1968, **24**.

[7] T. J. Hardwick, *Canad. J. Chem.*, 1957, **35**, 428.

[8] H. N. Po and N. Sutin, *Inorg. Chem.*, 1968, **7**, 622.

[9] (*a*) A. E. Cahill and H. Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 2312; (*b*) L. B. Anderson and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 1470.

The possibility of the formation of Fe^{IV} ion in the course of Fe^{II} oxidation by H_2O_2 [9] cannot be excluded; however, the free radical mechanism, namely reactions (1)—(2), is well supported by substantial evidence gathered over the last decade (especially using the e.s.r. technique). Recently, more transition metal ions, such as chromium(II) and vanadium(IV), in their reaction with H_2O_2, were found to yield secondary radicals in the presence of organic substrates.

Since the knowledge of the rate of reaction (1) at different pH values is of considerable importance in view of work done recently in our laboratory,[10] where it is stressed that ignorance of this value induced some workers into erroneous interpretations when considering the active species in these ' Fenton-like ' systems, we found it worthwhile to study the kinetics of the reduction of H_2O_2 in the acid range by chromium(II), titanium(III), and vanadium(IV). No intention was made here to draw any conclusions concerning the various ionic species, either of the metal ion or H_2O_2, present in the reaction mixtures and experimental conditions were chosen as similar as possible to those usually used in experiments where the e.s.r. flow technique is used.

EXPERIMENTAL

Solutions of hydrogen peroxide, vanadium(IV), titanium(III), and chromium(II) were prepared, under nitrogen, and determined as described previously.[10] Acidities were adjusted using AnalaR perchloric or sulphuric acid.

All pH measurements were done with a Beckman H3 pH meter. The kinetics of reaction (1) were studied at 25 °C under pseudo-first order conditions, using the stopped-flow technique. The stopped-flow apparatus has been described elsewhere.[11] The reactions were followed spectrophotometrically through the decay of the reactants or *via* the appearance of the reaction products. No attempt was made to keep the ionic strength constant, since we were interested only in determining the rate of the reactions under similar conditions to those generally used with the e.s.r. flow technique.

The pulse radiolysis technique was used to study reaction (2) at room temperature. A Varian V-7715 linear electron accelerator giving 5 MeV electron rectangular pulses with 200 mA current was used as a radiation source. Pulse length was approximately 0·2 µs. A Spectrosil irradiation cell, 4 cm long, with an optical path of 12 cm, was used. The analysing light source was a 150 W Xenon arc lamp. Further details of the experimental assembly are given elsewhere.[12] All the solutions were deaerated in 100 ml syringes before irradiation, by bubbling ultra-pure argon for at least 10 min.

RESULTS AND DISCUSSION

Reaction of M^{n+} *with* H_2O_2

Chromium(II).—The oxidation of Cr^{II} by H_2O_2 has been shown to proceed *via* a one electron oxidation mechanism [*i.e.* reactions (1) and (2)], by analysis of the Cr^{III} reaction product.[13] Further support for that mechanism can be found in the fact that, during Cr^{II} oxidation by H_2O_2, the same secondary radicals are formed by reaction of OH radicals with various organic substrates regardless of the source of the OH radicals.[10a] An adoption of a free-radical mechanism for the oxidation of Cr^{II} by H_2O_2 contradicts the conclusions of Cahill and Taube [9a] but fits later results of Anderson and Plane [9b] who re-employed the ^{18}O-tracer technique when studying the path of the reaction.

We studied the oxidation of chromium(II) by H_2O_2, by following the change in optical density at 700 nm, where Cr^{II} does absorb, and at 230 nm, where both Cr^{II} and H_2O_2 absorb. Unfortunately, the signal-to-noise ratio was very low, due to the small change in absorbance and the high background absorption; hence, it was impossible to measure reliably the $[Cr^{II}]$ decay at its peak (700 nm). It was more convenient to study the reaction at 230 nm, although there was a large experimental error even at this wavelength. However, the data obtained using an excess of Cr^{II}, gave pseudo-first-order plots from which k_1, the second-order rate constant was calculated.

Under the experimental conditions where $[Cr^{II}] \gg [H_2O_2]$, it would be reasonable to assume (see paragraph 2) that reaction (1) is followed immediately by reaction (2). Hence, the $[Cr^{II}]$ decay might be represented by the rate law:

$$\frac{d[M^{n+}]}{dt} = 2k_1[M^{n+}][H_2O_2] \qquad (5)$$

On the other hand, at $[H_2O_2] > [Cr^{II}]$, reactions (6)—(8) might take place concurrently:

$$OH + H_2O_2 \xrightarrow{k_6} HO_2 + H_2O \qquad (6)$$

$$HO_2 + HO_2 \xrightarrow{k_7} H_2O_2 + O_2 \qquad (7)$$

$$HO_2 + M^{n+} \xrightarrow{k_8} M^{(n+1)+} + HO_2^- \qquad (8)$$

Indeed, the decay of $[Cr^{II}]$ at $[H_2O_2] > [Cr^{II}]$ fits neither first nor second order mechanism. Therefore, the rate constants were calculated only from experiments where $[H_2O_2] < [Cr^{II}]$. The results are presented in the Table. A similar value of k_1 was obtained on replacing the acid with H_2SO_4.

Titanium(III).—The only attempt to study the $Ti^{III} + H_2O_2$ reaction was done indirectly by Florin *et al.*[14] They followed the appearance of the peroxy-complex of titanium(IV) which follows [15] reaction (1):

$$Ti^{IV} + H_2O_2 \longrightarrow Ti^{IV}\text{–}H_2O_2 \qquad (9)$$

thus obtaining a value of $200 M^{-1} s^{-1}$ as a lower limit for k_1. k_1 Was also estimated [10a] using the e.s.r. method, on adding organic substrate to the reaction mixture, and

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[10] (*a*) G. Czapski, A. Samuni, and D. Meisel, *J. Phys. Chem.*, 1971, **75**, 3271; (*b*) G. Czapski, *ibid.*, p. 2957.

[11] G. Czapski and A. Samuni, *Israel J. Chem.*, 1969, **7**, 361.

[12] Internal Report of Accelerator Lab. Hebrew Univ., Jerusalem, Israel.

[13] H. Taube and H. Meyers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

[14] R. E. Florin, F. Sicillio, and L. A. Wall, *J. Phys. Chem.*, 1968, **72**, 3154.

[15] M. Orhanovic and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1967, **89**, 278.

following the secondary organic radicals formed. However, no direct investigation of the primary reaction of Ti^{III} with H_2O_2 has been done.

We mixed titanium(III) solution with H_2O_2 and measured, using the stopped-flow technique, the change in the absorbance of the reaction mixture at 230 nm, keeping $[H_2O_2] < [Ti^{III}]$, in order to prevent optical density changes due to reaction (9). The pH dependent rate constant of reaction (9) has been measured in both $HClO_4$ and H_2SO_4 and was found to be at most 125 and 590 $M^{-1}s^{-1}$ respectively,[15] in the range of acidity used here. Therefore a proper choice of the concentrations enabled us to eliminate the interference of reaction (9). Indeed each run was also studied at 410 nm (the absorption peak of Ti^{IV}–H_2O_2) where no change in absorption due to formation of peroxytitanium(IV) complex was detected. Under these experimental conditions, expression (5) was again adopted for the $[Ti^{III}]$ decay rate. We verified this assumption by adding 0·5M propan-2-ol to the reaction mixture. In such a solution most OH radicals will react with the alcohol, thus decreasing the apparent decay rate. Indeed the addition of the alcohol did cut down the decay rate by a factor of two, as expected.

Second order rate constants for the reduction of H_2O_2 by metal ions, in $HClO_4$ at 25 °C

Metal ion	$[M^{n+}]_0$ (mM)	$[H_2O_2]_0$ (mM)	pH	k_{obs}/s^{-1} *	$k_1/M^{-1}\ s^{-1}$	$k_1 M^{-1}\ s^{-1}$ average
Chromium(II)	3·5	0·17	1	$2{\cdot}0 \times 10^2$	$(2{\cdot}8 \pm 0{\cdot}7) \times 10^4$	$(2{\cdot}8 \pm 0{\cdot}7) \times 10^4$
Titanium(III)	5·4	0·36	0	3·0	$(2{\cdot}7 \pm 0{\cdot}2) \times 10^2$	$(2{\cdot}7 \pm 0{\cdot}3) \times 10^2$
	10·8	0·36	0	6·1	$(2{\cdot}8 \pm 0{\cdot}2) \times 10^2$	
	26	0·36	0	13·0	$(2{\cdot}5 \pm 0{\cdot}2) \times 10^2$	
	0·42	40·8	1	0·22	5·4 ± 0·5	5·8 ± 0·6
	0·42	61·2	1	0·31	5·1 ± 0·5	
Vanadium(IV)	0·42	136	1	0·81	6·0 ± 0·6	
	0·84	272	1	1·40	5·2 ± 0·5	
	0·84	543	1	3·4	6·3 ± 0·6	
	0·84	815	1	5·3	6·5 ± 0·6	

* k_{obs} = Pseudo first order rate constant.

$k_{[Ti^{III}+H_2O]}$ Was calculated from the pseudo-first order plots and the results are summarised in the Table. The results are in accordance with the indirect computation of k_1 done in our laboratory[10] using the e.s.r. technique. (The value previously quoted[14,16] as given by Chance,[17] refers to k_9 rather than to k_1.)

On comparing the values of k_1 and k_9[15] it is evident that unless $[Ti^{III}] > [H_2O_2]$, reactions (1) and (9) take place concurrently, hence keeping $[Ti^{III}] > [H_2O_2]$ is a requisite to prevent the formation of the long-lived intermediates known as S_1 and S_2 through reactions (10) and (11):

$$Ti^{IV}\text{–}H_2O_2 + OH \longrightarrow S_1,S_2 + OH^- \quad (10)$$

$$Ti^{IV}\text{–}H_2O_2 + HO_2 \longrightarrow S_1,S_2 + HO_2^- \quad (11)$$

resulting in a perturbation on the system, especially towards the end of reaction (1).

The effect of change of pH on k_1 was studied by the same method and the results are given in Figure 1. In $HClO_4$ solutions, k_1 increases with increasing pH and this behaviour will be seen to be a common phenomenon for all the 'Fenton-like' reagents. Our measurements were restricted to quite a narrow range of pH, since Ti^{IV} tended to precipitate at pH > 2 and blocked the observation cell. No buffer was used in spite of the fact that pH might change during the reaction; but this change was negligible in the pH range studied in view of the initial high H^+ concentrations, compared to $[H_2O_2]$.

Also given in Figure 1 are values of k_1 measured in sulphuric acid. The value of k_1 at the higher acid concentration, is appreciably higher than that measured in $HClO_4$, and no pH dependence was observed in the pH range studied. This might reflect the higher stability of the sulphate complex. A similar difference between $HClO_4$ and H_2SO_4 was found[15] in the reaction of complexation of Ti^{IV} with H_2O_2 [*i.e.* reaction (9)].

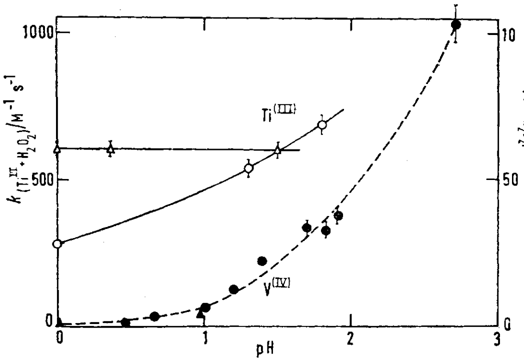

FIGURE 1 $k_{(M^{n+}+H_2O_2)}$ as a function of pH

Dashed line, $[V^{IV}]_0$ = 3mM $[H_2O_2]_0$ = 0·285M; solid line, $[Ti^{III}]_0$ = 54 mM $[H_2O_2]_0$ = 0·2 mM; circles, in $HClO_4$; triangles, in H_2SO_4

Vanadium(IV).—The oxidation of vanadium(IV) to vanadium(V) is accompanied by a generation of mono- and di-peroxyvanadium(V) complexes,[15] even in the absence of an excess of H_2O_2, as follows:

$$VO_2^+ + H_2O_2 \longrightarrow VO(O_2)^+ + H_2O \quad (12)$$

$$VO(O_2)^+ + H_2O_2 \longrightarrow VO(O_2)_2^- + 2H^+ \quad (13)$$

The kinetics of reaction (1) were studied by following the decay of $[V^{IV}]$ at 730 nm as well as the appearance of

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[16] C. E. Burchill, *J. Phys. Chem.*, 1971, **75**, 167.

[17] B. Chance, *J. Franklin Inst.*, 1940, **229**, 737.

the peroxy-complexes of vanadium(v) at their isosbestic point (404 nm). Working at $[H_2O_2] < [V^{IV}]$ resulted in the appearance of vanadium(v)–peroxy complexes even before all V^{IV} was oxidised to V^{V}. The fast formation of $VO(O_2)^+$ and $VO(O_2)_2^-$ absorption at 404 nm by reaction (12) was proceeded by its slow decay by the reaction of the excess of V^{IV} ions with these complexes. In order to eliminate the interference of reactions (12) and (13), we kept $[H_2O_2] > [V^{IV}]$ and used the appearance of V^{V}–peroxy-complex as a measure of the rate of reaction (1). Since $k_{12} \geqslant 1000$,[15] which is appreciably higher than k_1, such an approach is justified.

The results are presented in the Table. One would expect to observe deviations from the first order plot under the above mentioned experimental conditions due to the following reasons: (*a*) reaction (1) is rapidly followed by reactions (12) and (13) which results in a considerable change in acidity. This perturbation was negligible at pH $< 2{\cdot}5$ but was appreciable at higher pH where the uncertainty of pH during the reaction is rather high. In order to minimise this effect we kept $[V^{IV}]_0$ as low as possible. (*b*) V^{IV}, H_2O_2, and peroxy-vanadium complexes compete for the OH radicals, formed in the primary step, as the concentration of V^{IV} was at least 2 orders of magnitude less than that of H_2O_2, while k_2 is only greater by a factor of 20 than k_6. The rate equation for $[V^{IV}]$ will thus be given by

$$\frac{d[V^{IV}]}{dt} = k_1[V^{IV}][H_2O_2] \qquad (14)$$

rather than by expression (5), since the OH radicals will mainly react through reaction (6). This assumption was checked by the addition of 0·25M propan-2-ol to the reaction mixture. In such a case all the OH radicals will react with the organic substrate yielding alcoholic radicals, according to:

$$(CH_3)_2CHOH + OH \longrightarrow (CH_3)_2COH + H_2O \qquad (15)$$

Where $k_{15} = 1{\cdot}2 \times 10^9 M^{-1} s^{-1}$ [18] competition for OH radicals between reactions (2) and (15) would lead to an effective decrease in the $[V^{IV}]$ decay rate, when adding propan-2-ol. Since no such effect has been observed, we conclude that the decay rate of $[V^{IV}]$ at an excess of H_2O_2 is consistent with expression (14). Indeed, the first order plots, both in presence and absence of propanol-2-ol, were very satisfactory, indicating that the only reaction by which V^{IV} is oxidised is reaction (1). Dependence of k_1, for V^{IV}, on pH is given in Figure 1. k_1 Increases with increasing pH, as was found in the case of Ti^{III} and in the case of Fe^{II}.[6]

Reaction of M^{n+} *with* OH

The reaction of OH + M^{n+} was studied using the pulse radiolysis technique. It is commonly accepted that the ' primary products ' of the radiolysis of aqueous solutions are:

$$H_2O \rightsquigarrow e_{aq}^-, H, OH, H_2, H_2O_2 \qquad (16)$$

In acid solutions e_{aq}^- will be converted into H atoms by their reactions with hydrogen ions and will not compete in reaction with M^{n+}. The H atoms are not expected to react fast with M^{n+} ions, and even if they do react the absorption of these products is liable to appear only at shorter wavelengths than used here. This assumption was verified by the lack of any observable absorptions at 475 nm (the wavelength to be used) when solutions of M^{n+} without CNS^- were irradiated. Since the yield of H_2O_2 is only about 0·7 molecules/100 eV and since its reactivity with the ions investigated is much slower than that of the reactivity of OH, no interference of reaction (1) need be considered.

The fact that neither M^{n+} nor $M^{(n+1)+}$ have appreciable absorption bands in the convenient wavelengths forced us to choose the competition method as a probe to study reaction (2). Thus SCN^- and M^{n+} were allowed to compete for OH radicals. The product of the oxidation of thiocyanate, *i.e.* $(SCN)_2^-$, is produced by reactions (17) and (18) and can be easily followed at $\lambda_{max.} = 475$ nm ($\varepsilon_{475} = 7600 M^{-1} cm^{-1}$):

$$SCN^- + OH \longrightarrow SCN + OH^- \qquad (17)$$

$$SCN + SCN^- \rightleftharpoons (SCN)_2^- \qquad (18)$$

The yield of $(SCN)_2^-$ should change as a function of the concentrations of thiocyanate and M^{n+}, according to equation (19):

$$G(SCN_2^-) = G_{OH}\frac{k_{17}[SCN^-]}{k_{17}[SCN^-] + k_2[M^{n+}]} \qquad (19)$$

provided that enough thiocyanate ions are present to shift equilibrium (18) to the right. In such a case 1/o.d. at $\lambda = 475$ nm should depend linearly on the relative concentrations of the competing solutes:

$$\frac{1}{\text{o.d.}} = \frac{1}{\text{o.d.}_0}\left(1 + \frac{k_2[M^{n+}]}{k_{17[SCN^-]}}\right) \qquad (20)$$

where o.d._0 is the optical density at the same wavelength in the absence of M^{n+}.

Complications could arise while using this competition method since thiocyanate ions form complexes with the metal ions used here:

$$M^{n+} + SCN^- \overset{K_{21}}{\rightleftharpoons} (MSCN)^{(n-1)+} \qquad (21)$$

The values of K_{21} for $M^{n+} = VO^{2+}$ and $M^{n+} = Cr^{II}$ are 8·3 and $10{\cdot}1 M^{-1}$ [19] respectively. Thus, at $[SCN^-] = 10^{-3}M$ and $[M^{n+}] < 10^{-2}M$, [20] less than 8% of the thiocyanate ion could be complexed at the highest concentrations of the metal ions used in these experiments. The value of K_{21} for $M^{n+} = Ti^{III}$ is unknown in the literature but we could put an upper limit for it. This was done by observing the complex spectrum (peaking at about 550 nm with $\varepsilon_{550} = 12 M^{-1} cm^{-1}$) at $[Ti^{III}] = 0{\cdot}045M$ and $[SCN^-] = 0{\cdot}1M$, or $[SCN^-] = 1M$, against a reference cell containing $0{\cdot}045M$ Ti^{III}. From the absorbances thus

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[18] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493.

[19] S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, 1951, **73**, 4582.

[20] K. B. Yatsiminskii and T. I. Fedorova, *Izvest. Vysshikh Uchebnykh Zavedenii Khim.*, 1958, **3**, 40.

obtained, 0·08 and 0·54 (optical path of 1 cm) for the two thiocyanate concentrations, respectively, we could estimate $K_{21} \leqslant 2$. It is evident, therefore, that complexation effect in these systems is negligible. [The same argumentation holds if Ti^{IV} gives higher complexes with SCN^-, of the type $Ti(SCN)_n{}^{3-n}$].

Results for competition between the various M^{n+} ions and SCN^- agree quite well with expression (20) as can be seen in Figure 2. Thiocyanate concentration was held constant at 1 mM. [Since $K_{18} = 2 \times 10^{-5}$,[21] less than 1% of SCN radicals would not be converted to $(SCN)_2^-$.]

As the pulses used were about 0·2 μs long, yielding less than 4 μM radicals, and since the o.d. was measured at the end of the pulse, the values obtained are at a time where reactions (17) and (18) are completed, while recombination reactions of $(SCN)_2^-$ and/or H atoms are negligible. Indeed $(SCN)_2^-$ decayed with a half-life greater than 0·1 ms. On addition of either Ti^{III} or V^{IV}, no effect on the decay kinetics of $(SCN)_2^-$ could be observed. On the other hand, reaction between Cr^{II} and $(SCN)_2^-$ (or SCN) was quite appreciable; nevertheless, $(SCN)_2^-$ yields were determined in that case by extrapolation of its trace to the middle of the pulse.

Results in Figure 2 refer to experiments performed at 0·1M $HClO_4$. From the slopes of Figure 2 we get $k_2/k_{17} = 0{\cdot}023$, 0·11, and 0·44 for V^{IV}, Ti^{III}, and Cr^{II} respectively and taking Baxendale's [21] value for $k_{17} = 2{\cdot}8 \times 10^{10}$ M^{-1} s^{-1} one gets $k_2 = (6{\cdot}4 \pm 0{\cdot}4) \times 10^8$, $(3{\cdot}0 \pm 0{\cdot}3) \times 10^9$, and $(1{\cdot}2 \pm 0{\cdot}2) \times 10^{10}$ M^{-1} s^{-1} for the three metal ions respectively. Repeating the same experiment with V^{IV} but in 0·2N H_2SO_4, we found that $k_2 = 5{\cdot}9 \times 10^8$ M^{-1} s^{-1} which is practically the same as that in perchloric acid.

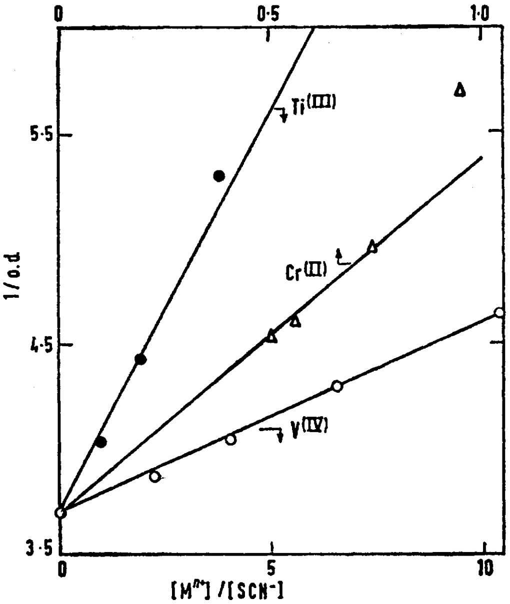

FIGURE 2 Variation of $(SCN)_2^-$ yields with $[M^{n+}]$ on pulse irradiating acid deaerated solutions of 1 mM NaSCN in the presence of chromium(II), titanium(III), and vanadium(IV) ions, at various concentrations

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[21] J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, 1969, 2389.