Pulse Radiolysis of Titanium(III) and Other Metal(III) Ions in the Presence of Formic Acid

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Oxidation of titanium(III) to titanium(IV) by hydroxyl radicals is observed on pulse radiolysis of titanium(III) solutions at pH 1·4 in the absence of formic acid. In the presence of 1·0M-formic acid the formate radical CO_2H ($pK_a = 1{\cdot}4$) is produced first, and titanium(III) is subsequently reduced to titanium(II), $k = ca.\ 5 \times 10^6$ l mol^{-1} s^{-1} at room temperature, pH 1·4. Under the same conditions this radical also reduces europium (III), but not ytterbium(III), chromium(III), or scandium(III). Reduction of scandium(III) is not observed at pH 4·2—4·9 in the absence of formic acid.

THIS work was initiated as part of a study to obtain more information regarding the properties of titanium(II) in aqueous solution. Compounds of bivalent titanium are few in number and the ion has at present no known aqueous chemistry. Attempts to prepare solutions of titanium(II) by electrolytic reduction of aqueous titanium(III) chloride and sulphate solutions, $[H^+] = 10^{-2}$M, $I = 0{\cdot}02$—$0{\cdot}20$M, using a cell which is satisfactory for the production of ytterbium(II) (oxygen-free conditions, mercury-pool cathode *ca.* 15 cm^2, 0·02—

0·07 A, 5—8 V)[1] were unsuccessful. Oxidation of titanium(II) by water is generally assumed to be rapid.[2] It was therefore decided to investigate by pulse radiolysis the conditions under which reduction of titanium(III) to titanium(II) occurs. To test the procedure adopted, the reduction of other metal(III) ions, the (II) oxidation states of which are known to exist in aqueous solution, were also studied under similar conditions. It was also of interest to us whether any evidence could be obtained for the existence of scandium(II).

Nature of Problem.—The radiolysis of water can be described by equation (1). At moderate solute concen-

$$H_2O \rightsquigarrow e_{aq}^-, H, OH, H_2, H_2O_2, H^+ \qquad (1)$$

trations and in neutral solutions values of G, the molecular yield per 100 eV of absorbed energy, are generally in the region $G_e = 2{\cdot}6$ (for e_{aq}^-), $G_H = 0{\cdot}60$, $G_{OH} = 2{\cdot}6$, $G_{H_2} = 0{\cdot}45$, and $G_{H_2O_2} = 0{\cdot}75$. However for the strongly acidic conditions used in the present studies, solvated electrons are rapidly converted to H atoms, and yields are $G_H = 3{\cdot}6$ and $G_{OH} = 2{\cdot}9$.* Competition between (2) and (3) is therefore observed,

$$e_{aq}^- + H^+ \longrightarrow H \qquad (2)$$

$$e_{aq}^- + M^{III} \longrightarrow M^{II} \qquad (3)$$

An additional process which is sometimes observed is the reduction of metal ions by H atoms. Rothschild and Allen report a rate constant $2{\cdot}2 \times 10^7$ l mol^{-1} s^{-1} for the reduction of iron(III) by H atoms.[4] For metal ions as used in this study having (II) oxidation states which are strongly reducing, it is unlikely that this step will make a significant contribution. Oxidation by OH can also be observed if the (III) state is not readily reduced and the (IV) state of the metal is reasonably stable. Thus in a recent study[5] with praseodymium(III), the (IV) state was formed exclusively.

RESULTS

Pulses of 2 μs duration were used and the dose per pulse varied between 4 and 16 krad, so that *ca.* (1—5) × 10^{-5}M-concentrations of both e_{aq}^- and OH radicals were produced. All studies were at room temperature (25 ± 2 °C).

Titanium(III) *in the Absence of Formic Acid.*—Hexaaquotitanium(III) has an acid dissociation constant *ca.* 2×10^{-3} mol l^{-1} at 25 °C,[6] and to avoid precipitation of titanium(III) it is necessary to work at pH <3. Pulse radiolysis under these conditions results in little if any reduction of titanium(III). The increase in absorption in the ultraviolet region was attributable to reaction (4),

$$Ti^{III} + OH \longrightarrow Ti^{IV} + OH^- \qquad (4)$$

Thus on pulsing 10^{-3}—10^{-2}M-solutions of titanium(III) sulphate in 0·02M-sulphuric acid the shape of the spectrum in the region 250—350 nm was the same as that observed for a solution of titanium(IV) sulphate at [H$^+$] = 0·02M.[7] Absorption coefficients ($\varepsilon = 420$ l mol^{-1} cm^{-1} at 250 nm) were in satisfactory agreement assuming a value $G(Ti^{IV}) = G_{OH} = 2{\cdot}9$. A rate constant ($3{\cdot}0 \times 10^9$ l mol^{-1} s^{-1}) has recently been reported for the reaction of titanium(III) with OH.[8]

Formic Acid Solutions.—Most of the studies were at pH 1·4 when formic acid (pK_a = 3·75 at 25 °C)[9] is essentially undissociated. Micic and Markovic[10] have reported that e_{aq}^- reacts with HCO_2H by two paths to give H and HCO_2^-, and the formyl radical and OH^- as primary products [see (5)]. The HCO radical

$$HCO_2H + e_{aq}^- \begin{cases} \longrightarrow HCO_2^- + H \\ \longrightarrow HCO + OH^- \end{cases} \qquad (5)$$

is likely to react with HCO_2H to give formaldehyde and the formate radical,[11] and H atoms react with formic acid as in equation (6). Reaction (7) is also effective. Thus e_{aq}^-,

$$HCO_2H + H \longrightarrow CO_2H + H_2 \qquad (6)$$

$$HCO_2H + OH \longrightarrow CO_2H + H_2O \qquad (7)$$

H, and OH react with formic acid to give the formate radical which behaves as a strong reducing agent [see equation (8)].[12] The pK_a value for the formate radical

$$CO_2H - e^- \longrightarrow CO_2 + H^+ \qquad (8)$$

is *ca.* 1·4.[13] Most of the present work was carried out at or near to pH 1·4, when concentrations of CO_2H and the radical ion CO_2^- are approximately equal. The end of pulse absorption in the absence of metal ions is entirely due to CO_2H/CO_2^-. Since the rate constant for (6) is $1{\cdot}1 \times 10^6$ l mol^{-1} s^{-1}, we chose to use 1M-formic acid in the first instance so that the full yield of CO_2H was observed at the end of the pulse. It follows that under these conditions $G(CO_2H/CO_2^-)$ is given by $G(e_{aq}^-) + G(H) + G(OH) = 6{\cdot}5$. Recent work has shown that the ultraviolet spectra of CO_2H and CO_2^- are similar, with maximum absorption at 250 ± 5 nm, but that absorption coefficients of the two species differ.[13] At pH 1·4 the absorption coefficient has been determined and is *ca.* 1600 l mol^{-1} cm^{-1}. The decay of the CO_2H/CO_2^- absorption at pH 1·4 obeyed second-order kinetics, rate constant

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* A summary of rate constants for pulse radiolysis studies is given by Anbar and Neta.[3]

[1] Procedure as used by R. J. Christensen and J. H. Espenson, *Chem. Comm.*, 1970, 756; personal communication from Professor J. H. Espenson.

[2] See for example F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' Wiley, New York, 3rd edn., 1972, p. 816.

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

[4] W. G. Rothschild and A. O. Allen, *Radiation Res.*, 1958, **8**, 101.

[5] M. Farraggi and A. Feder, *J. Chem. Phys.*, 1972, **56**, 3294.

[6] R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, 1962, **1**, 155; M. R. Paris and C. L. Gregoire, *Analyt. Chem. Acta*, 1968, **42**, 439; and H. Krentzien and F. Brito, *Chem. Abs.*, 1970, **73**, 7865b. See also comments in ref. 7.

[7] For details of preparation see J. D. Ellis and A. G. Sykes, *J.C.S. Dalton*, 1973, 537.

[8] A. Samuni, D. Meisel, and G. Czapski, *J.C.S. Dalton*, 1972, 1273.

[9] H. S. Harned and N. D. Embree, *J. Amer. Chem. Soc.*, 1934, **56**, 1042; M. Lloyd, V. Wycherley, and C. B. Monk, *J. Chem. Soc.*, 1952, 4363.

[10] O. I. Micic and V. Markovic, *Internat. J. Radiation Phys. Chem.*, 1972, **4**, 43.

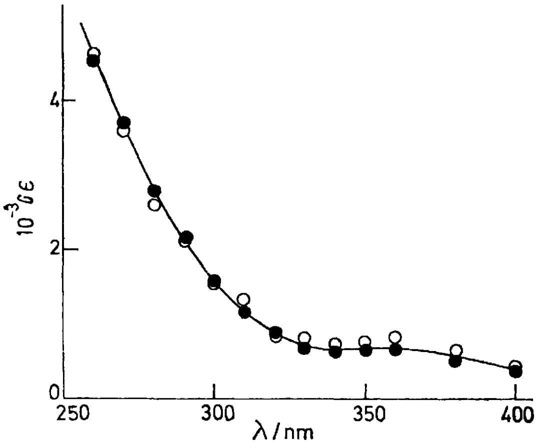
[11] D. Smithies and E. J. Hart, *J. Amer. Chem. Soc.*, 1960, **82**, 4775.

[12] G. V. Buxton, F. S. Dainton, and D. R. McCracken, *J.C.S. Faraday I*, 1973, **69**, 243.

[13] G. V. Buxton and R. M. Sellers, *J.C.S. Faraday I*, 1973, **69**, 555.

ca. $1{\cdot}2 \times 10^{9}$ l mol^{-1} s^{-1}. No permanent absorption was observed following this decay.

Titanium(III) *in the Presence of Formic Acid*.—The possibility that titanium(II) is produced on pulse radiolysis of titanium(III) in the presence of formic acid is dependent on whether CO_2H and/or CO_2^- are able to reduce titanium(III). Concentrations used were such that OH reacted with HCO_2H [equation (7)] in preference to titanium(III). With 1M-formic acid, pH 1·4, the end of pulse absorption remained essentially unchanged on increasing the titanium(III) from 10^{-3} to 10^{-2}M (a *ca.* 20% decrease in intensity was observed). The decay of the absorption was however accelerated by increasing the titanium(III) and the dose per pulse, and a long-lived ($t_{\frac{1}{2}}$ *ca.* 1·8 ms) absorption remained (see Figure). The intensity of this long-lived absorption increased with increasing concentration of titanium(III), decreased with increasing dose per pulse and with decreasing pH, but remained unchanged when the formic acid was decreased from 1 to 0·1M. These observations are consistent with the initial absorption being due to CO_2H/CO_2^- and the long-lived absorption to a reduced form of titanium(III), which we believe to be titanium(II). The decrease in the intensity of the initial absorption at the higher titanium(III) concentration is probably due to titanium(III) competing with H^+ for e_{aq}^-, or with HCO_2H for H, or both, during the pulse and to the fact that the ε_{250} for the final product is less than ε_{250} for CO_2H/CO_2^-. Kinetic analysis of the decay is consistent with competition between reactions (9)



Ultraviolet spectrum of titanium(II) at pH 1·4 in 1M-formic acid (●), spectrum independent of initial titanium(III) concentration, and in 0·1M-formic acid, (○).

$$CO_2H\ (\text{or } CO_2^-) + CO_2H\ (\text{or } CO_2^-) \longrightarrow \text{products} \qquad (9)$$

$$CO_2H\ (\text{or } CO_2^-) + Ti^{III} \longrightarrow Ti^{II} + CO_2 + H^+ \qquad (10)$$

and (10).* If it is assumed that CO_2H and CO_2^- react with titanium(III) at the same rate, the rate constant for (10) is *ca.* 5×10^{6} l mol^{-1} s^{-1}. The decrease in intensity of the long-lived absorption which is observed on increasing hydrogen-ion concentrations is consistent with CO_2^- reacting the faster.

Other experiments in which 1M-formic acid was replaced by 1M-methanol gave an end of pulse $G\varepsilon$ which was slightly increased in the presence of 10^{-2}M-titanium(III). After 100 μs, $G\varepsilon_{260}$ was only one-tenth that in the formic acid system. In this case the radicals CO_2H and CO_2^- are replaced by CH_2OH for which ε_{260} is *ca.* 500 l mol^{-1} cm^{-1},[14] and the results obtained are as expected if CH_2OH does not react with titanium(III).

Stock solutions of titanium(III) sulphate in sulphuric acid were used because titanium(III) reacts appreciably with perchlorate ions.[15] When solutions of titanium(III) chloride in 0·02M-HCl were pulsed with 0·1—1·0M-formic acid an additional species Cl_2^-, $\varepsilon_{max.} = 1{\cdot}25 \times 10^{4}$ l mol^{-1} cm^{-1} at 340 nm,[16] was formed [see equations (11) and (12)]. The

$$OH + Cl^- \longrightarrow OH^- + Cl \qquad (11)$$

$$Cl^- + Cl \longrightarrow Cl_2^- \qquad (12)$$

decay of Cl_2^- at 380 nm was monitored and gave a first-order dependence on Cl_2^- and on titanium(III) (2×10^{-3}—8×10^{-3}M). The reaction is believed to be as in equation (13) and the rate constant *ca.* 4×10^{8} l mol^{-1} s^{-1}. In

$$Ti^{III} + Cl_2^- \longrightarrow Ti^{II} + 2Cl^- \qquad (13)$$

sulphate solutions no evidence was obtained for the reaction of OH with HSO_4^- to give HSO_4 (ε = *ca.* 10^{3} l mol^{-1} cm^{-1} at 450 nm).[17]

Other Metal Ions in the Presence of Formic Acid.—All experiments were at pH 1·4 and in the presence of 1M-formic acid. With 5×10^{-4}—5×10^{-3}M-europium(III) the stable spectrum of europium(II) (peak *ca.* 250 nm, $\varepsilon = 1600$ l mol^{-1} cm^{-1})[18] was obtained. Because of the similarity of spectra of europium(II) and CO_2H/CO_2^- it was not possible to obtain a precise rate constant, $k \gg 7 \times 10^{6}$ l mol^{-1} s^{-1}. In the absence of formic acid the formation of europium(II) was very much reduced, as expected if reaction (3) only is effective and europium(II) is re-oxidized by OH radicals.

No CO_2H/CO_2^- reduction of 10^{-2}M-solutions of ytterbium(III), chromium(III), and scandium(III) was observed. However some reduction of chromium(III) to chromium(II) by e_{aq}^- was apparent, and subsequent changes could be accounted for by reaction (14). The same changes were

$$CO_2H\ (\text{or } CO_2^-) + Cr^{II} \longrightarrow CrCO_2H^{2+} \qquad (14)$$

apparent when solutions of chromium(II) (2×10^{-4}M) in 1M-formic acid, pH 1·4, were pulsed, rate constant $(1{\cdot}1 \pm 0{\cdot}1) \times 10^{9}$ l mol^{-1} s^{-1}. Cohen and Meyerstein[19] have recently reported rate constants ($3{\cdot}4 \times 10^{7}$—$2{\cdot}5 \times 10^{8}$ l mol^{-1} s^{-1}) for the reactions of a range of alkyl radicals with chromium(II). Features of spectra of the products are absorption maxima at *ca.* 270—310 nm and absorption coefficients of *ca.* 1000—3000 l mol^{-1} cm^{-1}.[19] A similar spectrum was observed in this study for reaction (14). Accordingly we suggest that the product of reaction (14) resulting from the chromium(II) reduction of CO_2H/CO_2^- has a chromium–carbon bond, and that the chromium is in formal oxidation state (III).[20]

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* At low pH values as used in this study the products are HCO_2H and CO_2, at higher pH values oxalate ions are also produced.

[14] P. Wardman, Ph.D. Thesis, University of Leeds, 1967.

[15] F. R. Duke and P. R. Quinney, *J. Amer. Chem. Soc.*, 1954, **76**, 3800.

[16] M. Anbar and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 3829.

[17] E. Heckel, A. Henglein, and G. Beck, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 149; A. K. Pikaev and V. I. Zolotareuskii, *Izvest. Akad. Nauk. U.S.S.R.*, 1967, 188.

[18] F. D. S. Butement, *Trans. Faraday Soc.*, 1948, **44**, 667; M. Faraggi and Y. Tendler, *J. Chem. Phys.*, 1972, **56**, 3287.

[19] H. Cohen and D. Meyerstein, *J.C.S. Chem. Comm.*, 1972, 320.

[20] See also W. Schmidt, J. H. Swinehart, and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 1117.

Solutions of (0·3—3·0) × 10^{-4}M-scandium(III) in water, $[H^+]$ = (1·4—5·6) × 10^{-5}M,* were pulsed in the absence of formic acid. First-order rate constants obtained for the decay of the e_{aq}^- absorption at 575 nm were entirely accounted for by reaction (2) (rate constant 2 × 10^{10} l mol^{-1} s^{-1}). It is concluded that there is no reaction of scandium(III) with e_{aq}^- under these conditions.

DISCUSSION

The experiments described clearly indicate a reaction between titanium(III) and CO_2H/CO_2^-. Since the latter is a strong reducing species, titanium(II) would seem the most likely product. The rate constant observed (*ca.* 5 × 10^6 l mol^{-1} s^{-1}) is appreciably faster than that for the complexing of thiocyanate with titanium(III) (*ca.* 8 × 10^3 s^{-1} at 25°),[22] and for the water exchange of titanium(III) (*ca.* 10^5 s^{-1} at 25°),[23] after allowing for ion-pair formation, and for this reason is probably outer sphere. An inner-sphere reaction similar to that illustrated in equation (14) and yielding the titanium(IV) species $TiCO_2H$ with titanium–carbon bonding seems unlikely therefore. Moreover, if this reaction were a possibility, the CH_2OH radical would be expected to react in the same way. No reaction of titanium(III) was apparent however on pulsing in the presence of 1M-methanol. We therefore feel justified in excluding formation of $TiCO_2H$.

The titanium(II) spectrum obtained in this study has $G\varepsilon_{260}$ = *ca.* 4600, and assuming $G(Ti^{II}) \ngtr 6{\cdot}5$ it follows that titanium(II) has $\varepsilon_{260} \nless 700$ l mol^{-1} cm^{-1}. Since experiments were in 1M-formic acid it is important to consider possible effects of formate in the inner-co-ordination of the titanium(II). To this end we have recorded spectra 250—400 nm first of all for titanium(III) and iron(III), pH 1·4, with and without addition of 1M-formic acid, and obtained evidence in the case of iron(III) for a strong (formate→metal) charge-transfer band, $\lambda_{max.}$ = 280 nm. In the case of titanium(III) a shoulder was observed at 270—290 nm. With cobalt(II), manganese(II), vanadium(II), and chromium(II) on the other hand, 1M-formic acid (pH 1·4) had no effect on the shape of spectra 250—400 nm, and no charge-transfer bands, or bands directly attributable to the formate ligand, were observed. Formic acid/formate solutions absorb at 209 nm, ε = *ca.* 50 l mol^{-1} cm^{-1}. The spectrum shown in the Figure is expected to be the same as that for hexa-aquotitanium(II) even though some formate is present in the inner-co-ordination sphere. This is further substantiated by the experiments in the presence of 0·1M-formic acid, when the spectrum is the same as in 1·0M-formic acid.

It has been found that CO_2H/CO_2^- reduces titanium(III) and europium(III), but not ytterbium(III), chromium(III), or scandium(III). From standard oxidation potentials,[24] chromium(III) would be expected to be the most readily reduced. However the outer-sphere interconversion of chromium(III) and chromium(II) is unfavourable, and requires high reorganization energy due it is believed to the tetragonal distortion of high-spin chromium(II). The CO_2H/CO_2^- reduction of chromium(III), like all Cr^{2+} outer-sphere reactions, is probably slow for this reason. An inner-sphere reduction is excluded by the substitution inertness of chromium(III).

Dainton and James[25] have shown that for the elements of the first transition series from vanadium to nickel, a straight line is obtained when the standard oxidation potential of the M^{II}/M^{III} couple is plotted against the long-wavelength limit of the electron-transfer spectrum of the M^{2+} ion. The standard reduction potential of the Ti^{2+}/Ti^{3+} couple in aqueous solution has been estimated at −1·29 V.[26] On this basis the charge-transfer spectrum of titanium(II) would be expected to reach quite far into the visible region. This would seem to be borne out by the titanium(II) spectrum obtained in this study. We note also that the absorption at 260 nm is more intense than that observed with other oxidation state (II) ions in the first transition series.[25] The peak at λ = *ca.* 360 nm may be a *d–d* transition ($^3T_{1g} \longrightarrow {}^3A_{2g}$) superimposed on c.t. bands. It is unfortunate that the procedure used in these studies does not enable other less intense *d–d* bands in the visible range to be measured. The visible spectrum of Ti^{2+} ions in a sodium chloride crystal has recently been reported,[27] so that information is now available concerning both the ultraviolet and visible spectrum of titanium(II).

EXPERIMENTAL

Titanium(III) sulphate solutions were prepared by dissolving 0·5 g of titanium hydride (Fluka AG, >99·5% purity) in 10 ml of 2·5M-sulphuric acid at 50—55 °C. The process required *ca.* 4 h after which the solution was filtered in air through a No. 4 (fine) Pyrex glass sinter, and diluted six-fold with argon-degassed distilled water. To remove titanium(IV) this solution was reduced under air-free conditions, at a mercury-pool cathode until the absorption at the titanium(III) visible peak remained constant (*ca.* 3 h required, 6 V, 0·3 A). The concentration of titanium(III) was determined by addition of an excess of cerium(IV) and back titration with iron(II). The concentration of hydrogen ion was determined by exchanging the titanium(III) for hydrogen-ion on a cation-exchange column, and then titrating the eluant with standard sodium hydroxide solution. Typical concentrations were $[Ti^{III}]$ = 0·07M and $[H^+]$ = 0·45M. In the presence of this amount of sulphate the peak position for titanium(III) is at 518 nm and ε = 3·94 l mol^{-1} cm^{-1}. Titanium(III) chloride solutions in hydrochloric acid were prepared using a similar procedure. For a solution $[Cl^-]$ = 0·45M the peak position of

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* The acid dissociation constant for scandium(III) is given by Kilpatrick and Pokras.[21] No account was taken of dimer formation in calculating the value of $[H^+]$.

[21] M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, 1954, **101**, 39.

[22] H. Diebler, *Z. phys. Chem.*, 1969, **68**, 64.

[23] A. M. Chelnick and D. Fiat, unpublished work, quoted in D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, 1968, **90**, 608.

[24] W. M. Latimer, ‘ Oxidation Potentials,’ Prentice-Hall, New York, 2nd edn., 1952.

[25] F. S. Dainton and D. G. L. James, *Trans. Faraday Soc.* 1958, **54**, 649.

[26] D. R. Rosseinsky, *Chem. Rev.*, 1966, **66**, 467.

[27] E. Smith, *J.C.S. Chem. Comm.*, 1972, 1121.

titanium(III) is at 503 nm and $\varepsilon = 3{\cdot}98$ l mol^{-1} cm^{-1}. Standard syringe techniques were used for the transference of titanium(III) solutions under air-free conditions.

Solutions *ca.* 10^{-2}M of europium(III), ytterbium(III), and scandium(III) were made up by weight by dissolving Eu_2O_3 (Rare Earth Products Ltd., 99·9%), Yb_2O_3 (Johnson and Matthey, Specpure grade), and $Sc_2(SO_4)_3$ (Alfa Inorganics, 99·9%) in 2·0M-perchloric or sulphuric acid, and diluting as required. To prepare the chromium(III) solutions, Cr_2O_3 (May and Baker, 99% reagent) dissolved in 5·0M-perchloric acid was reduced with an excess of 100 volume hydrogen peroxide (AnalaR grade). The solution was left for 2 h when *ca.* 0·1 g of platinum black was added to catalyse the decomposition of the excess of hydrogen peroxide. The solution was set aside overnight, after which the platinum black was filtered off. Solutions obtained were *ca.* 0·4M in chromium(III) ($\varepsilon_{max.} = 15{\cdot}6$ l mol^{-1} cm^{-1} at 408 nm) and *ca.* 1·0M in perchloric acid. Solutions of chromium(II) perchlorate in perchloric acid were prepared by the electrolytic reduction of chromium(III) under oxygen-free conditions using the procedure previously described in work from these laboratories.

All solutions for pulse radiolysis experiments were made up in water which had been triply distilled first from acidified dichromate and then from alkaline permanganate solutions. The formic acid used was AnalaR grade.

The pulse radiolysis technique has been described previously.[28-30] A 2·9 MeV electron beam from a Van de Graaff accelerator was used as the high-energy source in this study. The beam was incident on an air-free sample (*ca.* 1·5 ml) of the solution under investigation, contained in a rectangular cell with Spectrosil quartz windows and radiation depth 7 mm. The optical path length of the cell was 10 mm. Absorption by the solution was detected by passing light from a Xenon-arc source through the cell at right-angles to the electron beam. The dosimetry factor was determined using a 5×10^{-3}M-potassium ferrocyanide solution saturated with oxygen ($G\varepsilon = 3200$ at 420 nm for potassium ferricyanide). For most of this study doses in the range 5—12 krad were used.

Spectra were recorded over the range 240—450 nm using band widths of 5 and 10 nm. In the presence of formic acid, the absorption at a particular wavelength was recorded immediately after the pulse and again after *ca.* 60 μs when the decay of the CO_2H radical was complete. The kinetics of the decay of the formate radical were followed at 260 and 320 nm.

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[29] L. M. Dorfman and M. S. Matheson, *Progr. Reaction Kinetics*, 1965, **3**, 238.

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