

Reactions of Benzophenone in its Triplet State with Aliphatic Substrates: Hydrogen Isotope Exchange, Formation of Organochromium(III) Species, and Related Reactions

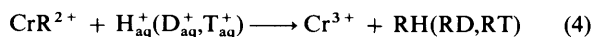
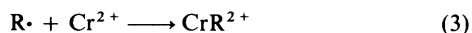
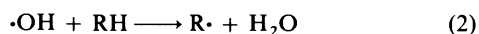
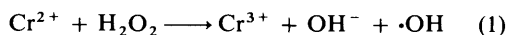
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U.v. irradiation (for up to 20 min) of benzophenone in 54% (v/v) dioxane–water in the presence of chromium(II) trifluoromethanesulphonate results in the formation of the penta-aquadioxanylchromium(III) complex. The complex is thought to arise from the trapping by Cr^{II} of dioxanyl radicals which are the result of H-atom abstraction by ³Ph₂CO* from dioxane. On prolonged irradiation (1 h) in the presence of tracer quantities of tritiated water, the products are Cr(H₂O)₆³⁺ and tritium-labelled dioxane, formed by reaction of the penta-aquadioxanylchromium(III) complex with hydronium ions present in the solution. When the irradiation of benzophenone and chromium(II) trifluoromethanesulphonate is carried out in 54% (v/v) tetrahydrofuran–water and in 54% (v/v) 1,2-dimethoxyethane–water, the more acid-stable penta-aquachromium(III) complexes derived from tetrahydrofuran and 1,2-dimethoxyethane are formed.

Free radicals derived from saturated (including alicyclic) organic compounds can be reduced to the corresponding carbanions or carbanion-like species by metal ions in low oxidation states.^{1,2} This reduction plays a role in the radiation-induced hydrogen-isotope exchange which can be observed on β- or γ-irradiation of aqueous solutions of the compounds.³ The first chemical process in these exchange reactions is the radiolytic formation of hydroxyl radicals and hydrogen atoms. The further reaction of these species with the organic substrate leads to organic radicals by hydrogen abstraction. Reaction of the reduced carbanion (or carbanion-like species) with a proton (deuteron or triton) donor completes the exchange event.³

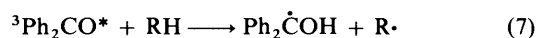
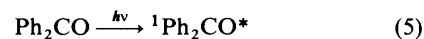
Similar hydrogen-exchange reactions are observed when hydroxyl radicals are generated with analogues of Fenton's reagent based on reducing transition metal ions.⁴ The reduction of the radical by the metal ion may be a simple outer-sphere electron transfer, but, in the course of investigating the mechanism of this reduction in more detail for Cr^{II} ions, we found the mechanism to involve an organochromium species. Under the influence of acid this species releases the organic starting material (with hydrogen exchange if it occurs in an isotopically different aqueous solution). The entire reaction sequence can be written as in equations (1)–(4). The



intermediacy of the organochromium compounds in the exchange reaction can in favourable cases be demonstrated by isolating them from reaction systems of low acidity. Their reaction with aqueous acid [equation (4)] can then be studied separately.

The involvement of Cr^{II} ions in these exchange reactions is complicated because they take part in two reaction steps, *viz.* reactions (1) and (3). We have therefore sought a simple and general method for generating organic radicals from RH precursors by a process that does not rely on the preparatively unattractive high-energy irradiation used in our early studies³ nor involve reducing metal ions at any stage before reaction (3).

These considerations have led us to examine the triplet state of benzophenone as a possible convenient route to organic radicals and hence to organochromium(III) species. These studies are now reported. The mechanism of the reaction envisaged involves steps (5)–(7). Walling and Gibian⁵ found



the u.v.-irradiation of benzophenone in cyclohexane to yield bicyclohexyl and 1,1,2,2-tetraphenylethane-1,2-diol, in agreement with the foregoing scheme. The products formed during a similar irradiation of an aqueous solution of benzophenone⁶ were consistent with the reaction of the benzophenone triplet with water, giving hydroxyl radicals and the diphenylhydroxymethyl radical as precursors to the detected products.

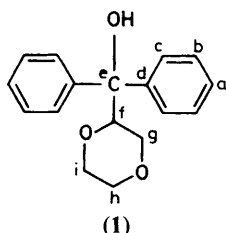
In order to apply reactions (5)–(7) in our study it was found necessary to select a solvent system that incorporated water but which also was a good solvent for benzophenone and was itself a suitable substrate for the formation of radicals. For this reason the present investigations centre on a dioxane–water mixture as reaction medium, with some related subsidiary studies including the use of tetrahydrofuran and 1,2-dimethoxyethane. As far as possible, the behaviour of these systems was related to the earlier studies with the Fenton system, so as to test some of the mechanistic inferences from that work.⁴

Experimental

Materials.—Dioxane, tetrahydrofuran, and 1,2-dimethoxyethane were each purified by refluxing with *ca.* 10% by volume of conc. hydrochloric acid for 3 h under nitrogen. After the addition of tin(II) chloride, reflux was continued for a further 3 h. The acid was then neutralised with solid potassium hydroxide, and the organic layer was separated and refluxed with sodium metal. The pure liquids were obtained by distillation under nitrogen. Benzophenone (m.p. 47–48 °C) was recrystallised from absolute alcohol. Solutions of chromium(II) trifluoromethanesulphonate were obtained by dissolving metallic chromium (previously washed with conc. hydrochloric acid and distilled water) in aqueous trifluoromethanesulphonic acid (*ca.*

3 mol dm⁻³) with gentle warming.⁷ Chromium(II) perchlorate solutions were prepared from chromium metal and aqueous perchloric acid (*ca.* 3 mol dm⁻³). The solutions prepared in this way were found to contain concentrations of Cr^{II} in the range 1.3–1.4 mol dm⁻³ as estimated spectrophotometrically.⁸ During the preparation and subsequent experiments, Cr^{II} solutions were rigorously protected from air oxidation and were handled in a nitrogen atmosphere.

Irradiation of Benzophenone in Dioxane and 54% (v/v) Dioxane-Water.—A solution of benzophenone (0.1 mol dm⁻³) in dioxane was irradiated with light of wavelength 340 nm by use of a medium-pressure mercury arc (Engelhard Hanovia) with a light filter consisting of aqueous nickel sulphate⁹ (0.36 mol dm⁻³). After irradiation for 20 h the solution was concentrated and filtered to remove solid 1,1,2,2-tetraphenylethane-1,2-diol which had precipitated. G.l.c. (Silicone OV-17 on Chromosorb W-HP) showed the filtrate to consist of several components. The major component was isolated by column chromatography on alumina with 7:6:2 (v/v) benzene–hexane–ethyl acetate as eluant and identified from its n.m.r. and mass spectra as 1,4-dioxan-2-yl(diphenyl)methanol (1), m.p. 115 °C; δ_H(CDCl₃) 7.18–7.57 (m, 10 H, arom.), 4.44 and 4.56 (dd, 1 H, C₁H), 3.34–3.88 (m, 6 H, C₂H, C₆H, C₅H); δ_C(CDCl₃) 145.54 (C_d), 128.18 (C_b), 127.01 (C_a), 126.54 (C_c), 125.43 (C_e), 77.40 (C_g), 66.96 (C_h), and 66.08 (C_i); *m/z* 269 (M⁺ – H, 68%), 252 (M⁺ – H₂O, 40), 183 (Ph₂COH⁺, 100), 105 (PhCO⁺, 98), 77 (Ph⁺, 92), and 51 (C₄H₃⁺, 68). 1,1,2,2-Tetraphenylethane-1,2-diol and 1,4-dioxan-2-yl(diphenyl)methanol were also the major products of irradiation of benzophenone in 54% (v/v) dioxane–water.



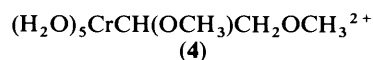
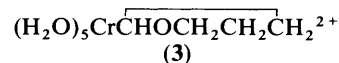
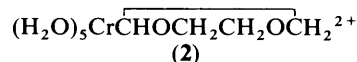
Irradiation of Benzophenone and Cr²⁺ in Aqueous Solution and in 54% (v/v) Dioxane-Water.—An aqueous solution of benzophenone (2.1 × 10⁻³ mol dm⁻³) was irradiated under nitrogen for 20 min using a low-pressure mercury arc (PCQ model 9G-1) with maximum output at 254 nm. The u.v. spectra of aliquots of the reaction solution removed during irradiation indicated that a species with λ_{max.} *ca.* 400 nm was formed and reached a maximum concentration after *ca.* 1 min. The spectral changes were small and difficult to reproduce. In view of this the experiments were repeated with 54% (v/v) dioxane–water as solvent in which much higher concentrations of benzophenone could be used.

A solution of benzophenone (0.1 mol dm⁻³) and chromium(II) trifluoromethanesulphonate (0.2 mol dm⁻³) in 54% (v/v) dioxane–water and under nitrogen was irradiated with light of wavelength 340 nm using a medium-pressure mercury arc with aqueous nickel sulphate (0.36 mol dm⁻³) as a light filter. A white precipitate of 1,1,2,2-tetraphenylethane-1,2-diol was formed during the irradiation. Aliquots of the reaction solution were removed and u.v. spectra showed that an intermediate with λ_{max.} *ca.* 390 nm was formed during irradiation and reached a maximum concentration after *ca.* 20 min. After irradiation for 1 h this species was no longer detectable and the colour of the solution had changed from the characteristic blue of Cr(H₂O)₆²⁺ to the green colour of Cr(H₂O)₆³⁺. The intermediate was identified as the penta-aquadioxanyl-

chromium(III) ion (see later). In order to purify and characterise the organochromium species, the reaction solution, after irradiation for 20 min, was transferred to an ion-exchange column (Dowex 50W-X8 Na⁺) which had been washed with aqueous sodium perchlorate (0.1 mol dm⁻³). All operations were carried out under nitrogen and the column was kept at 5 °C by passing cooled water through a jacket. After addition of the reaction solution, the column was washed with aqueous 0.1 mol dm⁻³ sodium perchlorate followed by 1.0 mol dm⁻³ sodium perchlorate. U.v. spectra of the collected fractions showed that the intermediate produced during irradiation was eluted with 1 mol dm⁻³ sodium perchlorate. These fractions were set aside for further study.

In similar experiments the irradiation of benzophenone and chromium(II) trifluoromethanesulphonate was carried out with 54% (v/v) tetrahydrofuran–water and with 54% (v/v) 1,2-dimethoxyethane–water as solvent. In each case, species with λ_{max.} *ca.* 390 nm were formed during irradiation for 25 min and aqueous solutions of the purified organochromium complexes were obtained by ion-exchange chromatography. It will be shown later that these species are the penta-aquachromium(III) complexes derived from tetrahydrofuran and from 1,2-dimethoxyethane. They were obtained in much higher yield than the dioxanylchromium(III) complex isolated in the experiments with 54% (v/v) dioxane–water as solvent.

Alternative Preparation of Penta-aquaorganochromium(III) Complexes.—The penta-aquaorganochromium(III) complexes derived from dioxane, tetrahydrofuran, and 1,2-dimethoxyethane were prepared by generating and trapping the appropriate organic radical by using an analogue of Fenton's reagent.^{2,4} Dioxane, tetrahydrofuran, or 1,2-dimethoxyethane was treated with Cr^{II}–H₂O₂ in a solvent mixture of the organic component with water. The complexes thus prepared are tentatively assumed to have the structures (2), (3), and (4)

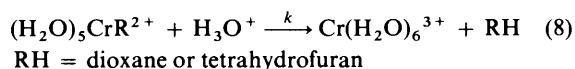


respectively but a plausible alternative to (4) is penta-aqua[(2-methoxy)ethoxymethyl]chromium(III). Because of this ambiguity, the complex obtained from 1,2-dimethoxyethane will be referred to as DME-chromium(III).

In a typical procedure, penta-aquadioxanylchromium(III) was prepared by adding aqueous chromium(II) trifluoromethanesulphonate (0.015 mol dm⁻³; 1.4 mol dm⁻³) and aqueous hydrogen peroxide (0.005 mol dm⁻³; 1.6 mol dm⁻³) to 8% (v/v) dioxane–water (2 cm³). The u.v. spectrum of the solution taken at various times was consistent with quite rapid formation of penta-aquadioxanylchromium(III). Assuming quantitative formation of the complex according to equations (1)–(3), a molar absorptivity at λ_{max.} 390 nm of ε 274 dm³ mol⁻¹ cm⁻¹ was calculated, in agreement with the value (ε 270 dm³ mol⁻¹ cm⁻¹) obtained for the complex generated by pulse radiolysis.¹⁰ Penta-aqua(tetrahydrofuran-2-yl)chromium(III) (λ_{max.} 390; ε 339) and DME-chromium(III) (λ_{max.} 390; ε 178) were prepared similarly and aqueous solutions of the complexes were obtained pure by ion-exchange chromatography.

Reactions of Organochromium Complexes with Electrophiles.—The organochromium species formed during the irradiation of benzophenone and Cr^{II} in organic solvent–water

mixtures were identified by studying their reactions with electrophiles and comparing the kinetic behaviour with that of organochromium complexes prepared independently. The reactions of photochemically prepared penta-aquadioxanylchromium(III) and penta-aqua(tetrahydrofuran-2-yl)chromium(III) with acid were studied in aqueous solution and that of the former also in various dioxane-water mixtures. Reaction rates were measured over a range of concentrations of perchloric acid, 0.04–0.2 mol dm⁻³ for the dioxanyl complex and 0.15–0.72 mol dm⁻³ for the tetrahydrofuran complex, at 25 °C and at ionic strength 1.0 mol dm⁻³ maintained by addition of sodium perchlorate. Decomposition of the complexes [equation (8)] was initiated by addition of a small volume of



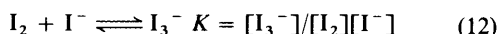
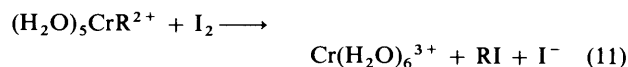
concentrated aqueous perchloric acid to a thermostatted solution of the complex ($3\text{--}8 \times 10^{-4}$ mol dm⁻³) and the course of the reaction was followed spectrophotometrically by observing the decrease in absorbance at 390 nm. The reactions were accurately first-order with respect to complex [equation (9)] and the absorption spectrum after complete reaction

$$-d[(\text{H}_2\text{O})_5\text{CrR}^{2+}]/dt = k_{\text{obs}}[(\text{H}_2\text{O})_5\text{CrR}^{2+}] \quad (9)$$

corresponded to that of the hexa-aquachromium(III) ion. The observed first-order rate coefficients (k_{obs}) were proportional to the stoichiometric concentrations of perchloric acid [or hydronium ions; equation (10)].

$$k_{\text{obs}} = k[\text{H}_3\text{O}^+] \quad (10)$$

The DME-chromium(III) complex prepared by reaction of Cr^{III}-H₂O₂ with 1,2-dimethoxyethane was found to remain unchanged in the presence of 4 mol dm⁻³ aqueous perchloric acid over 2 h. For benzylchromium(III) complexes it has been observed¹¹ that reaction with iodine [equation (11)] occurs



$$d[\text{I}_3^-]/dt = k[(\text{H}_2\text{O})_5\text{CrR}^{2+}][\text{I}_2] = k[(\text{H}_2\text{O})_5\text{CrR}^{2+}][\text{I}_3^-]/K[\text{I}^-] \quad (13)$$

more rapidly than reaction with hydronium ion. Accordingly, the reaction of DME-chromium(III) with iodine was investigated and it was observed that, in a solution of the chromium complex and iodine, a reaction occurred which involved the consumption of iodine. It is probable that this reaction is cleavage to give Cr(H₂O)₆³⁺ and CH₃OCHICH₂OCH₃, but for the purposes of the present work it was not necessary to establish its precise nature. The kinetics were studied in aqueous solution at 25 °C. The reaction was begun by adding a small volume of a solution of iodine and potassium iodide to a quartz cuvette containing an aqueous solution of the DME-chromium(III) complex (5×10^{-5} to 3×10^{-4} mol dm⁻³) with perchloric acid (0.5 mol dm⁻³) and sodium perchlorate (0.5 mol dm⁻³). Under conditions where iodine was present in deficit compared with penta-aquadioxanylchromium(III), the decrease in absorbance at 352 nm, due to removal of I₃⁻, was observed to be a first-order process [equation (14)], and values for the rate coefficient (k_{obs})

$$d[\text{I}_3^-]/dt = k_{\text{obs}}[\text{I}_3^-] \quad (14)$$

$$k_{\text{obs}} = k[(\text{H}_2\text{O})_5\text{CrR}^{2+}]/K[\text{I}^-] \quad (15)$$

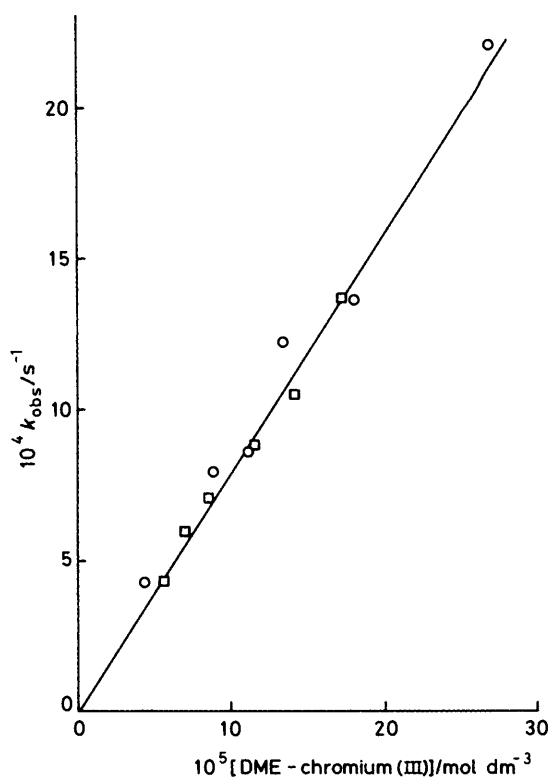


Figure. Kinetic data for the reaction of DME-chromium(III) with iodine; comparison of data points (□) for complex prepared photochemically and data points (○) for complex prepared by Fenton's reaction

were determined in the presence of varying concentrations of DME-chromium(III). The value of k_{obs} was proportional to the concentration of complex, as shown in the Figure.

Tritium Exchange.—Experiments were carried out to investigate the possibility of tritium exchange into dioxane during the irradiation of benzophenone and chromium(II) trifluoromethanesulphonate in 54% (v/v) dioxane-water in the presence of tracer levels of tritiated water. A reaction solution consisting of benzophenone (0.1 mol dm⁻³) and chromium(II) trifluoromethanesulphonate (0.05 mol dm⁻³), with tritiated water at activities of 5.9 to 23.6 mCi per 130 cm³, was irradiated for 1 h. The reaction mixture was filtered to remove 1,1,2,2-tetraphenylethane-1,2-diol and solid potassium carbonate was added. The upper (dioxane) layer was separated using Whatman IPS phase-separating filter paper and dried with solid potassium carbonate and then calcium hydride. The dioxane was purified by preparative g.l.c. (F & M Scientific Corp. Model 770) with a column of 20% Carbowax 20M on 80–100 mesh Celite. The purified dioxane was subjected to liquid scintillation counting, and activities varying from 20-fold to 80-fold above the level of background or control experiments were obtained depending upon the activity of tritiated water used (see Table).

Results and Discussion

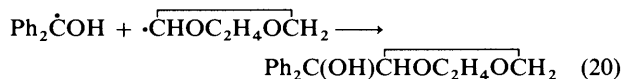
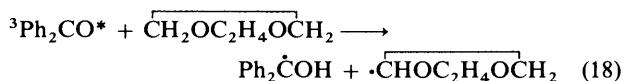
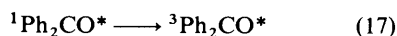
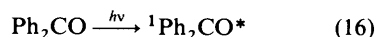
Photochemistry of Benzophenone in Dioxane and 54% (v/v) Dioxane-Water.—The irradiation of benzophenone in dioxane and in 54% (v/v) dioxane-water under our experimental conditions resulted in the formation of 1,1,2,2-tetraphenylethane-1,2-diol and 1,4-dioxan-2-yl(diphenyl)methanol⁴ (1) together with other (not identified) products. Previously, bicyclohexyl and 1,1,2,2-tetraphenylethane-1,2-diol were

Table. Tritium exchange during irradiation^a

Tritiated water activity (mCi)	Dioxane activity (disint. min ⁻¹ g ⁻¹)		Background count (disint. min ⁻¹)
	Before g.l.c.	After g.l.c.	
5.9	3 010 ± 130	2 703 ± 150	125
11.8	5 715 ± 160	5 382 ± 130	135
17.7	8 340 ± 100	8 150 ± 100	150
23.6	11 928 ± 250	10 836 ± 300	140
23.6 (Control A)	130 ± 35	118 ± 20	139
23.6 (Control B)	121 ± 25	108 ± 25	97
23.6 (Control C)	73 ± 10	58 ± 10	140

^a Reaction mixture consisted of 130 ml 54% (v/v) dioxane-water with benzophenone (0.1 mol dm⁻³) and chromium(II) trifluoromethanesulphonate (0.05 mol dm⁻³) irradiated for 1 h. In Control A benzophenone was omitted and in Control B chromium(II) trifluoromethanesulphonate was omitted. In Control C the mixture was not irradiated.

detected as the products of irradiation of benzophenone in cyclohexane.^{5,*} Evidence for the intermediate formation of the diphenylhydroxymethyl radical has been obtained from studies of the photolysis of benzophenone in aqueous solution.⁶ The following reactions account for the products detected in the irradiation in dioxane and 54% (v/v) dioxane-water.



Irradiation of Benzophenone in the Presence of Cr^{II} and the Formation of Organochromium(III) Complexes.—The absorption with λ_{max} 390 nm detected in the reaction mixture when benzophenone was irradiated in 54% (v/v) dioxane-water containing chromium(II) trifluoromethanesulphonate corresponds¹⁰ to that of the penta-aquadioxanylchromium(III) ion. This absorption reached a maximum under our conditions after 20 min. At this point the concentration of complex amounted to ca. 5% of the added benzophenone, taking the molar absorptivity as that of the complex that was prepared by Fenton's reaction and obtained in purified form as an aqueous solution in 1 mol dm⁻³ sodium perchlorate by ion-exchange chromatography. In addition to the evidence provided by the u.v. spectrum, confirmation that the intermediate was the penta-aquadioxanylchromium(III) ion was obtained by comparing the behaviour of the intermediate towards perchloric acid with that of penta-aquadioxanylchromium(III) prepared by reaction of Cr^{II}-H₂O₂ with aqueous dioxane. For both complexes the disappearance of the absorbance at 390 nm in the presence of excess of acid was a first-order process. The observed first-order rate coefficients (k_{obs}) were proportional to the acid concentration, and values for the second-order rate coefficient (k) for reaction with acid were obtained from equation (10). For the

complex generated photochemically the value $k = 0.38 \pm 0.03$ dm³ mol⁻¹ s⁻¹ was found for reaction in aqueous solution at 25 °C and ionic strength 1.0 mol dm⁻³. The hydrolysis of the complex generated from Cr^{II}-H₂O₂ and aqueous dioxane was studied in 8%, 31%, and 54% (v/v) dioxane-water, and values for the second-order rate coefficient (k) of 0.36 ± 0.01 , 0.27 ± 0.02 , and 0.045 ± 0.002 dm³ mol⁻¹ s⁻¹ respectively were obtained. These values are approximately linearly dependent on the mole fraction of dioxane. Linear extrapolation to aqueous solution gave a value for k of 0.46 ± 0.1 dm³ mol⁻¹ s⁻¹, in reasonable agreement with the result obtained for reaction of the species generated photochemically and with a previous value¹⁰ ($k = 0.48$ dm³ mol⁻¹ s⁻¹) obtained for penta-aquadioxanylchromium(III).

After irradiation for 1 h the penta-aquadioxanylchromium(III) complex was no longer detectable and the original blue colour of the solution due to Cr(H₂O)₆²⁺ was observed to have changed to the green of Cr(H₂O)₆³⁺. The disappearance of penta-aquadioxanylchromium(III) on prolonged irradiation is probably due to reaction with acid. The acid arises from dissociation of the chromium aquo ions and also from the added solution of chromium(II) trifluoromethanesulphonate which is prepared by dissolving metallic chromium in 3.0 mol dm⁻³ aqueous trifluoromethanesulphonic acid.

When the irradiation of benzophenone was carried out in aqueous solution in the presence of chromium(II) perchlorate, tentative evidence for the intermediate formation of a species with λ_{max} ca. 400 nm was obtained, although the reproducibility of the experiments was poor. It is possible that this species, which appeared to reach a maximum concentration after 1 min irradiation and became undetectable after a few minutes, is the penta-aqua(diphenylhydroxymethyl)chromium(III) ion. Owing to the limited solubility of benzophenone in water the complex would be formed in low concentration and this fact, combined with rapid decomposition, may explain why detection was difficult. Penta-aquaorganochromium complexes (H₂O)₅-CrR²⁺, in which R contains a hydroxy group, have been found to be exceptionally reactive compared with other organochromium complexes.² In such cases decomposition to RH and Cr(H₂O)₆³⁺ occurs by a pH-independent route as well as by a reaction with hydronium ion. For penta-aqua(hydroxymethyl)chromium(III), decomposition by the pH-independent route occurs with $t_{1/2}$ 17 min and for penta-aqua-(2-hydroxypropyl)chromium(III) $t_{1/2}$ 3 min is observed.² In addition, 2-hydroxyalkylchromium(III) complexes can undergo elimination in aqueous solution to give products¹³ other than RH and Cr(H₂O)₆³⁺. This high reactivity may explain why, in the present work, attempts to prepare aqueous solutions of penta-

* In recent studies of the irradiation of benzophenone in cyclohexane we have found cyclohexyldiphenylmethanol and diphenylmethanol as products in addition to 1,1,2,2-tetraphenylethane-1,2-diol and bicyclohexyl.¹²

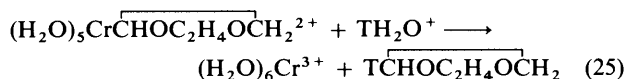
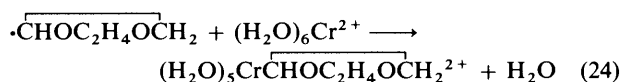
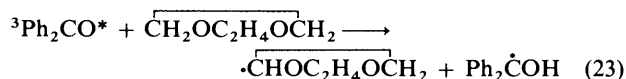
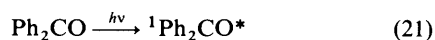
aqua(diphenylhydroxymethyl)chromium(III) by routes which have been used to prepare other organochromium(III) complexes were unsuccessful.

In the irradiation of benzophenone and chromium(II) trifluoromethanesulphonate in 54% (v/v) tetrahydrofuran-water, the penta-aqua(tetrahydrofuran-2-yl)chromium(III) ion was obtained. This was identified by studying the reaction of the complex with acid. A second-order rate coefficient of $3.6 \pm 0.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was obtained. This result is in good agreement with the value ($3.6 \pm 0.7 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) observed for the same reaction of the complex generated by reaction of $\text{Cr}^{\text{II}}-\text{H}_2\text{O}_2$ with aqueous tetrahydrofuran.

Irradiation of benzophenone and chromium(II) trifluoromethanesulphonate in 54% (v/v) 1,2-dimethoxyethane-water resulted in an organochromium complex (λ_{max} , 390 nm) which was stable over 2 h in aqueous perchloric acid (4 mol dm^{-3}). The DME-chromium(III) complex prepared by the reaction of $\text{Cr}^{\text{II}}-\text{H}_2\text{O}_2$ with 1,2-dimethoxyethane was also stable under these conditions. However both species reacted at the same rate with iodine in an overall second-order process. In the Figure, the observed first-order rate coefficients (k_{obs}) for the disappearance of tri-iodide ion in the presence of excess of complex are plotted against the concentration of complex; the points indicated as squares refer to the values of k_{obs} for the complex prepared photochemically and the circles refer to the complex generated by reaction of $\text{Cr}^{\text{II}}-\text{H}_2\text{O}_2$ with aqueous 1,2-dimethoxyethane.

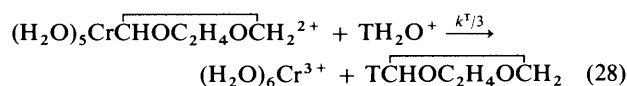
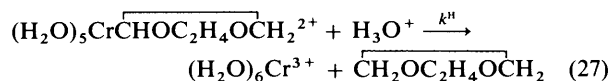
In the irradiation of benzophenone and chromium(II) in 54% (v/v) tetrahydrofuran-water and in 54% (v/v) dimethoxyethane-water much higher concentrations of the corresponding organochromium(III) complexes were obtained than in the irradiation using dioxane-water as solvent. This is accounted for by the greater reactivity of the dioxanylchromium complex towards acid.

Tritium exchange. Hydrogen-isotope exchange of RH in the presence of analogues of Fenton's reagent is thought to occur by the route shown in equations (1)–(4). Step (2) involves the generation of an organic radical by H-atom abstraction from RH by the hydroxyl radical, and this process is followed by trapping of the radical by Cr^{II} to form an organochromium(III) complex which on hydrolysis results in labelled RH and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. It is conceivable that a similar route for exchange can occur if organic radicals are generated photochemically in the presence of Cr^{II} . In support of this hypothesis it was found that the irradiation of benzophenone in the presence of chromium(II) trifluoromethanesulphonate in 54% (v/v) dioxane-water containing tritiated water at tracer levels led to tritium-labelled dioxane. In this experiment irradiation was continued for 1 h, during which time $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ is converted into $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. The extent of tritium incorporation into dioxane was found to be directly proportional to the concentration of tritiated water added to the reaction mixture (Table). A scheme which is compatible with the intermediate formation of penta-aquadioxanylchromium(III) during irradiation and with the incorporation of tritium into the solvent dioxane is shown in equations (21)–(25). The fate of the diphenylhydroxymethyl radical is not known, but reasonable possibilities are dimerisation to 1,1,2,2-tetra-phenylethane-1,2-diol and trapping to give penta-aqua(diphenylhydroxymethyl)chromium(III) which is hydrolysed to diphenylmethanol and hexa-aquachromium(III).



The tritium-exchange experiment was carried out with benzophenone in excess over chromium(II) trifluoromethanesulphonate. On the reasonable assumption that chromium(II) is equally effective in trapping dioxanyl and diphenylhydroxymethyl radicals, it is seen from equations (21)–(22) that half of the added chromium(II) will be converted into penta-aquadioxanylchromium(III), which will react as in equation (25). If the percentage exchange (E) into dioxane is defined by equation (26), the data in the Table give an average value for E of $3.06 \pm 0.07\%$. The value of E in an analogous experiment⁴ using $\text{Cr}^{\text{II}}-\text{H}_2\text{O}_2$ to bring about exchange into dioxane as in equations (1)–(4) was $3.7 \pm 0.3\%$. The similarity of these values supports the overall validity of the scheme in equations (21)–(25). The explanation¹⁴ for the low percentage exchange is a moderately large kinetic isotope effect ($k^{\text{H}}/k^{\text{T}}$) in the reaction of penta-aquadioxanylchromium(III) with acid [equations (27) and (28)].

$$E = 100 \times \frac{(\text{T}/\text{H}) \text{ in dioxane product}}{(\text{T}/\text{H}) \text{ in solvent H}_2\text{O}} \cdot \frac{[\text{dioxane}]}{[\text{Cr}^{\text{II}}]/2} \quad (26)$$



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References

- 1 D. Behar, A. Samuni, and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 2055; B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2174.
- 2 W. Schmidt, J. H. Swinehart, and H. Taube, *J. Am. Chem. Soc.*, 1971, **93**, 1117.
- 3 V. Gold and M. E. McAdam, *Proc. R. Soc. London, Ser. A*, 1975, **346**, 427, 443; *Acc. Chem. Res.*, 1978, **11**, 36.
- 4 V. Gold, S. M. Pemberton, and D. L. Wood, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1230.
- 5 C. Walling and M. H. Gibian, *J. Am. Chem. Soc.*, 1965, **87**, 3361.
- 6 M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 539.
- 7 H. Lux and G. Illman, *Chem. Ber.*, 1958, **91**, 2143.
- 8 J. P. Fackler and D. G. Holah, *Inorg. Chem.*, 1965, **4**, 954.
- 9 J. G. Calvert and J. N. Pitts Jr., 'Photochemistry', Wiley, New York, 1966, ch. 7, p. 687.
- 10 H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434.
- 11 J. C. Chang and J. H. Espenson, *J. Chem. Soc., Chem. Commun.*, 1974, 233.
- 12 A. Bakar bin Baba, V. Gold, and F. Hibbert, unpublished work.
- 13 H. Cohen, D. Meyerstein, A. J. Schusterman, and M. Weiss, *J. Am. Chem. Soc.*, 1984, **106**, 1876.
- 14 V. Gold and D. L. Wood, *J. Chem. Soc., Dalton Trans.*, 1981, 2452.

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