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J. Chem. Soc., Faraday Trans. 1, 1988, **84**(6), 2109–2127

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The Dehydrogenation of Ethanol in Dilute Aqueous Solution Photosensitised by Benzophenones

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The photochemical properties of a series of water-soluble benzophenones have been evaluated in dilute aqueous solution. The compounds possess lowest-energy singlet and triplet excited states demonstrating considerable n,π* character. As such, irradiation of the compounds in aqueous solution containing ethanol (2% v/v) results in pinacol formation *via* a triplet-state hydrogen-abstraction process. In the presence of a colloidal Pt catalyst, the intermediate ketyl and 1-hydroxyethyl radicals can be used to reduce water to H_2. The rate of H_2 formation and its total yield depend upon the nature of the substituent used to solubilise the benzophenone. The rate at which the ketyl radical transfers an electron to the Pt particles can be rationalised in terms of thermodynamic and electrostatic factors.

One of the best documented photochemical reactions concerns hydrogen abstraction from an alcohol by an electronically excited state possessing appreciable n,π* character.[1] The archetypal example of such a process is the irradiation of benzophenone in aqueous propan-2-ol:[2]

$$Ph_2CO^* + (CH_3)_2CHOH \rightarrow Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH$$

$$2Ph_2\dot{C}OH \rightarrow Ph_2C(OH)C(OH)Ph_2$$

$$2(CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CHOH + (CH_3)_2CO.$$

The intermediate ketyl radical has been identified by flash photolysis[3] and pulse radiolysis[4] techniques and, under most conditions, it undergoes rapid dimerisation to form a pinacol. Both ketyl[5] and 1-methyl-1-hydroxyethyl[6] radicals are reducing species which, in the presence of a suitable catalyst, should be able to reduce water to H_2. Thus, u.v.-irradiation of benzophenone in 1:1 water/propan-2-ol containing a Pt catalyst has been reported to generate H_2 with high quantum yield:[7]

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2.$$

This system[7] is remarkably simple but, of course, there are a few serious drawbacks as regards adapting it for a practical solar-energy storage device. The most obvious problems are that (1) near-u.v. light is required, (2) high concentrations of propan-2-ol are needed to solubilise the benzophenone and (3) the high rate of dimerisation of the ketyl radical necessitates high concentrations of a selective Pt catalyst to prevent pinacol formation.

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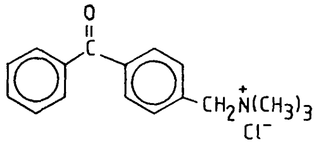
Water-soluble derivatives of benzophenone are now commercially available.[8,9] These materials can be prepared on an industrial scale and they are readily soluble in water. This means that low concentrations of alcohol can be used and, from an energy storage viewpoint, ethanol is preferred to propan-2-ol. Thus, a simple photosystem can be envisaged in which a water-soluble benzophenone derivative is used to dehydrogenate ethanol photochemically in dilute aqueous solution:

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2; \quad \Delta G^\circ = 42\ \text{kJ mol}^{-1}.$$

This paper describes the experimental findings relating to such a system, and compares a variety of benzophenone derivatives.

Experimental

The water-soluble benzophenones (**1**)–(**4**) were obtained from Ward Blenkinsop and used as received. Water was deionised and doubly distilled in a quartz still, whilst ethanol (Burroughs analytical grade) was used as received. Preparation of the Pt colloid has been described previously[10] and it has been fully characterised by high-resolution electron microscopy.[11]



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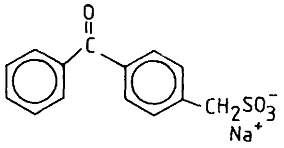

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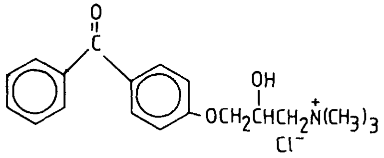

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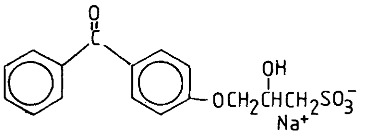

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Flash photolysis experiments were made with an N_2 laser (pulse duration 10 ns, maximum energy per pulse 15 mJ, excitation wavelength 337 nm) using N_2-purged aqueous solutions. Transient absorption spectra were measured point-by-point using an averaging procedure. Decay rate constants were measured at a fixed wavelength and have an expected accuracy of ±10%.

Cyclic voltammograms were recorded with a Rank E611 potentiostat driven by a purpose-built triangle-wave generator. Aqueous solutions of the benzophenone (1×10^{-3} mol dm^{-3}) containing KCl (0.2 mol dm^{-3}) and an appropriate buffer (10^{-3} mol dm^{-3}) were thoroughly purged with N_2. A glassy carbon working electrode was used in conjunction with a Pt counter-electrode and an SCE reference. Peak potentials had a reproducibility of ±5 mV.

Interaction between the ketyl radicals and colloidal Pt particles was studied by pulse

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radiolysis. A Febetron 705 accelerator was used to produce a single 50 ns pulse of 2 MeV electrons of *ca.* 600 rad. The aqueous solution of benzophenone derivative (5×10^{-4} mol dm^{-3}) containing 5% v/v propan-2-ol and phosphate buffer (10^{-3} mol dm^{-3}, pH 7) was thoroughly purged with N_2. Decay of the ketyl radical was monitored at 540 nm. Various amounts of freshly prepared Pt catalyst were added and the absorbance at 540 nm was analysed in terms of pseudo-first-order kinetics using a computer least-squares routine. At least four traces were averaged at each Pt concentration, and a minimum of three different concentrations were used. The bimolecular rate constants for interaction between the ketyl radical and Pt particles were derived from least-squares plots of the observed pseudo-first-order rate constants against total concentrations of Pt.

Steady-state irradiations were made with a 250 W xenon arc lamp filtered to remove i.r. and light of wavelength below 300 nm. Aqueous solutions of the benzophenone derivative (5×10^{-4} mol dm^{-3}) containing ethanol (2% v/v), acetate buffer (0.01 mol dm^{-3}, pH 4.7) and various amounts of colloidal Pt were thoroughly purged with N_2. The course of reaction was followed by absorption spectroscopy, and concentrations of evolved H_2 were determined by gas chromatography.[12] For all experiments, the solution (50 cm^3) was housed in a Pyrex cylindrical cell, with optical windows, of total volume 60 cm^3 fitted with a septum cap. Aliquots of solution or vapour (250×10^{-6} dm^3) were removed periodically and analysed. For quantum yield measurements, the light beam was passed through a Bausch and Lomb monochromator to isolate a 300 ± 15 nm window. The incident light intensity was measured by ferrioxalate actinometry.

Results and Discussion

Photophysical Properties

Spectroscopic studies[13] have indicated that the lowest excited singlet and triplet levels of benzophenone are of n,π^* character. In the ground-state absorption spectrum, the n,π^* transition is present only as a low-intensity tail that partially overlaps with the more intense π,π^* transition found at higher energy. Furthermore, it is known from the classical work of Porter and Suppan[14] that the energy of both n,π^* and π,π^* transitions depends on solvent polarity. In a polar solvent such as water, the n,π^* state is pushed to higher energy and the π,π^* state is lowered in energy. This effect tends to mix the two states in the various water-soluble benzophenones, making identification of the first excited singlet state somewhat unclear. From absorption spectroscopy in aqueous solution (fig. 1), the n,π^* transition can be seen clearly only for **1** and **2.** For the other compounds, it cannot be resolved from the π,π^* transition. However, in no case could room-temperature fluorescence be detected and the triplet excited state was formed with essentially unit quantum efficiency for all four compounds. This suggests that the first excited singlet state is of n,π^* character in each case.

The absorption spectra (fig. 1) show that the compounds absorb only a small fraction of the energy available in sunlight. The absorption maxima of the intense π,π^* transition occur at 257, 262, 289 and 312 nm, respectively, for compounds **1**–**4**. If we accept that the solar emission spectrum begins at 300 nm and that the highest concentration of compound that can be used is restricted to 10^{-3} mol dm^{-3} (see later) then the fraction of the energy available in sunlight that can be collected by these compounds is $< 5\%$. Clearly, this is incompatible with the genuine use of such compounds in solar-energy storage devices. However, the simplicity and relative efficiency of the systems at least partially compensate for the poor spectral features. Also, it is important to note that the photochemistry does proceed at reasonable rates in sunlight.

All the compounds showed low-temperature phosphorescence (see fig. 1) in aqueous ethanol. These spectra were well resolved, having typical lifetimes of *ca.* 5 ms, and

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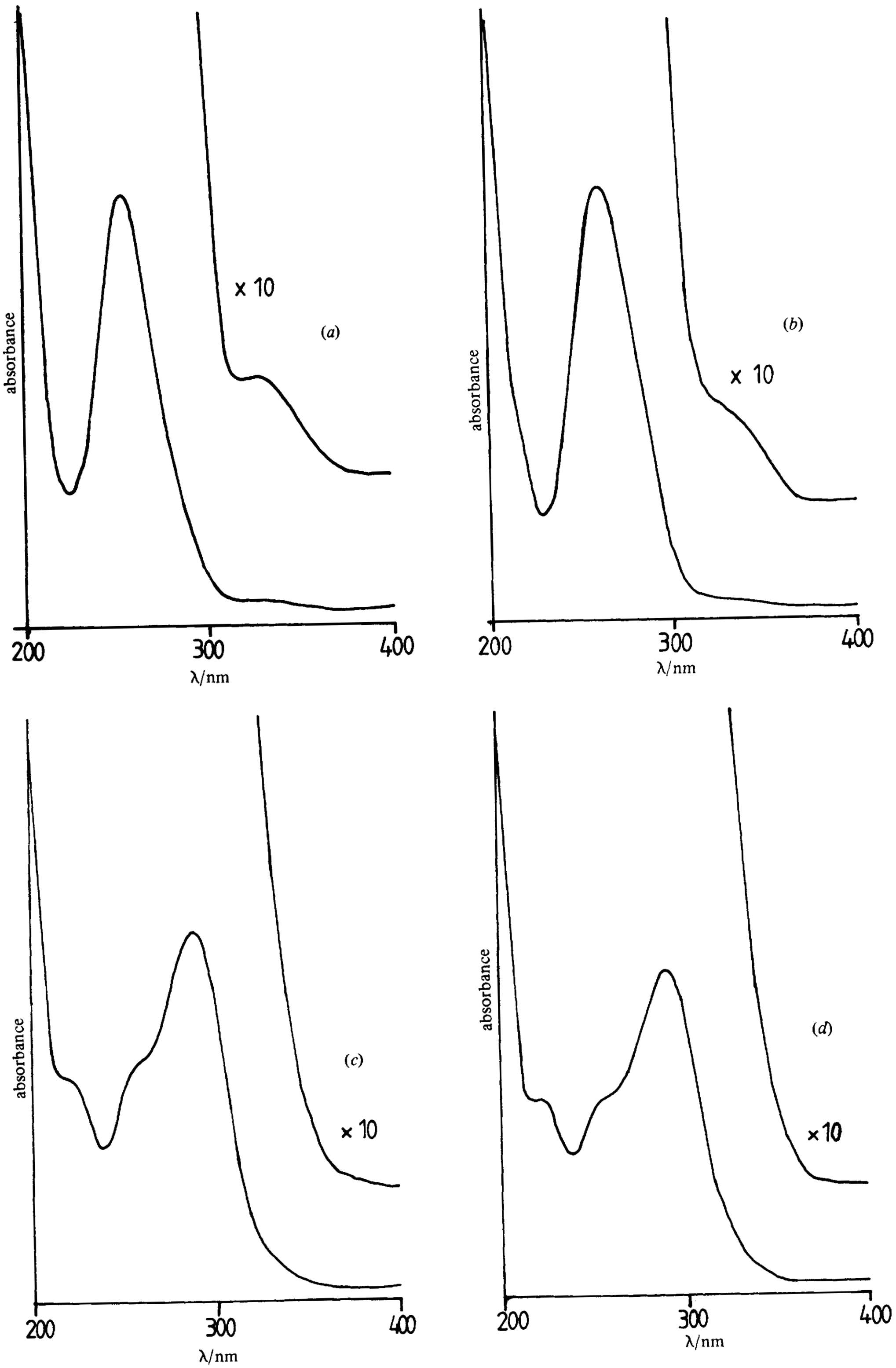

Fig. 1 (*a*)–(*d*). For caption see opposite.

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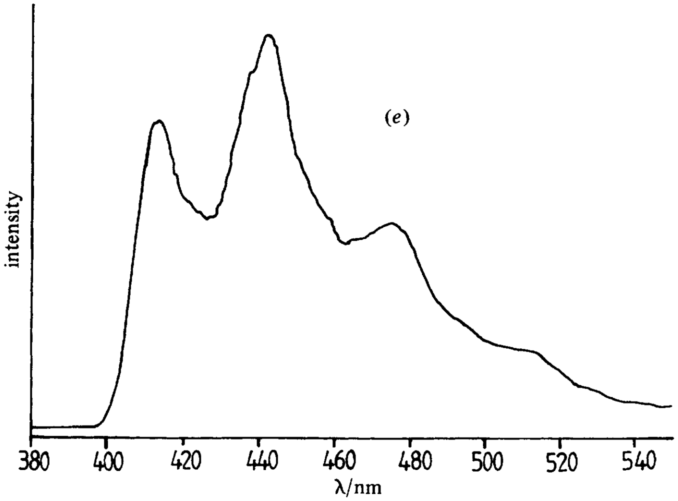

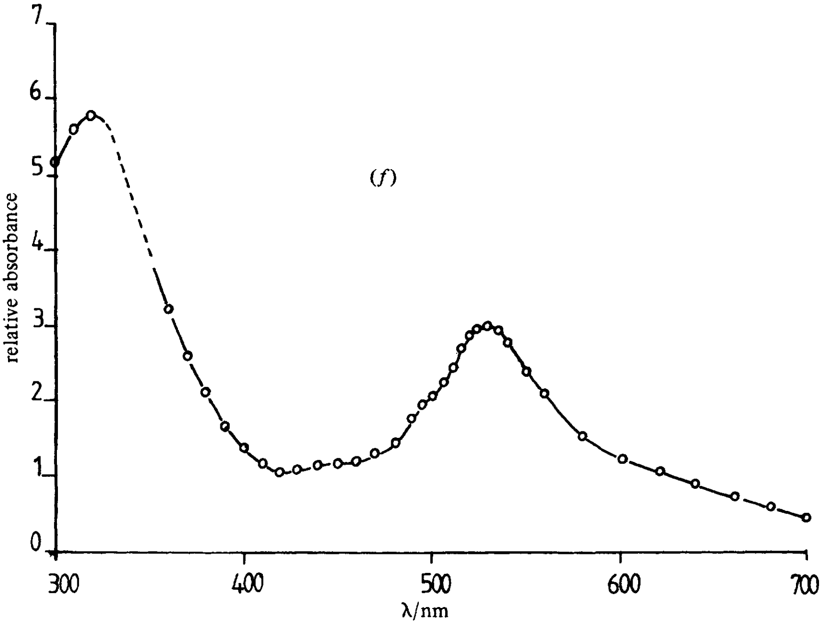

Fig. 1. Absorption spectra of the various benzophenone derivatives in neutral aqueous solution; (*a*) **1** ($\log \varepsilon_{257} = 4.24$), (*b*) **2** ($\log \varepsilon_{262} = 4.25$), (*c*) **3** ($\log \varepsilon_{289} = 4.15$) and (*d*) **4** ($\log \varepsilon_{312} = 4.11$). A phosphorescence spectrum recorded in aqueous ethanol at 80 K and a triplet absorption spectrum recorded 100 ns after flash excitation for **1** are shown in (*e*) and (*f*), respectively.

correspond to triplet energies of 280–290 kJ mol^{-1} (table 1). There are no obvious correlations between phosphorescence spectra and water-solubilising substituent, but all the observed spectra are consistent with the lowest-energy triplet excited state being of n,π^* character.

Intense triplet–triplet absorption, centred around 530 nm, was observed for all the compounds in outgassed aqueous solution. The observed triplet absorption spectra (fig. 1 contains a representative spectrum) are essentially identical to those published

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Table 1. Properties of the triplet excited states of the benzophenones in neutral solution

compound	E_t /kJ mol^{-1}	$k_0/10^4$ s^{-1}	$k_1/10^7$dm^3 mol^{-1} s^{-1}	τ_t /μs
1	287	3	5	15.2
2	283	3	8	9.0
3	289	4	30	3.2
4	278	—	50	1.8

previously[9,15] for benzophenone and compounds **1** and **2**. In aqueous solution, decay of the triplet excited state includes at least four pathways:

$$d[T]/dt = k_0[T]+k_1[T][BP]+k_2[T]^2+k_3[T][O_2].$$

Here, the inherent non-radiative decay rate constant for deactivation of the triplet excited state (k_0) cannot easily be separated from second-order rate constants for reaction between the triplet-state and ground-state compound (k_1), a second triplet (k_2) and oxygen (k_3). Using outgassed solutions and keeping the laser intensity low, decay of the triplet excited state could be described satisfactorily by first-order kinetics. The derived lifetimes depend on the total concentration of benzophenone [BP], showing the importance of self-quenching in these compounds. By varying the concentration of compound, estimates for k_0 and k_1 were obtained (table 1). It is seen that k_0 remains fairly insensitive to the nature of the substituent, but k_1 increases markedly when the substituent contains an easily abstractable hydrogen atom. This suggests that at least part of the mechanism for the self-quenching reaction involves hydrogen abstraction. Steady-state irradiation of compounds **3** and **4** in outgassed water does indeed result in destruction of the compounds. For compound **2**, previous work has found $k_1 = 7.3 \times 10^7$ dm^3 mol^{-1} s^{-1}, whilst benzophenone in water gave $k_1 = 1.2 \times 10^8$ dm^3 mol^{-1} s^{-1}.

Increasing the laser intensity results in an increase in the initial triplet concentration and introduces a considerable proportion of bimolecular process into the decay kinetics. At high triplet levels, analysis of the decay data was consistent with $k_2 = (4 \pm 1) \times 10^9$ dm^3 mol^{-1} s^{-1} for all the compounds. Similarly, addition of controlled amounts of O_2 gave an estimate for k_3 of $(3 \pm 1) \times 10^9$ dm^3 mol^{-1} s^{-1}. Overall, the flash photolysis experiments indicate that the maximum concentration of compound that should be used is *ca.* 1×10^{-3} mol dm^{-3}, whilst low-density light sources are needed to inhibit triplet–triplet annihilation. Using N_2-saturated aqueous solutions containing 1×10^{-3} mol dm^{-3} compound, the actual triplet excited state lifetimes (τ_t) were measured at low laser intensities and the derived values are collected in table 1.

Formation of the Ketyl Radical

For compounds **1** and **2** in N_2-saturated aqueous solution at pH 7, the triplet lifetime was measured as a function of the concentration of added ethanol. The triplet excited states of both compounds were quenched by ethanol with bimolecular rate constants (k_q) of $(5 \pm 2) \times 10^5$ dm^3 mol^{-1} s^{-1}. Previously,[9] it was reported that the triplet excited states of **1** and **2** were quenched by propan-2-ol with rate constants of 1.25×10^6 and 1.5×10^6 dm^3 mol^{-1} s^{-1}, respectively. In view of the lower CH bond dissociation energy for the tertiary H atom, propan-2-ol should be a better quencher than ethanol. The rate constant for reaction between triplet benzophenone and ethanol depends on the bulk solvent. In water,[16] k_q was found to be 2.4×10^6 dm^3 mol^{-1} s^{-1}, whereas values of 5.6×10^5 and 3×10^7 dm^3 mol^{-1} s^{-1}, respectively, have been found in pure ethanol[16] and fluorocarbons.[17]

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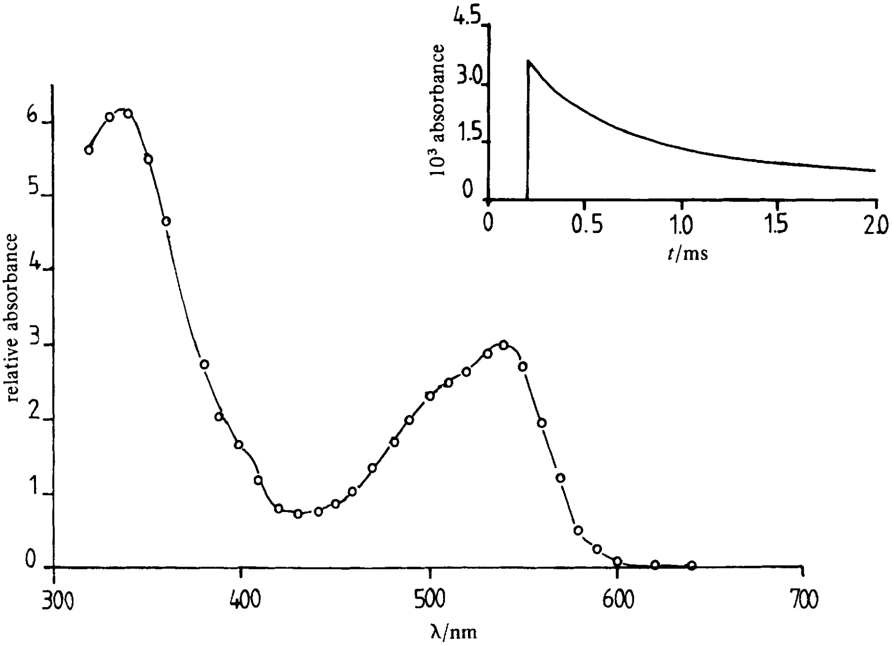

Fig. 2. Absorption spectrum of the ketyl radical as observed 0.1 ms after flash excitation of **1** in aqueous solution at pH 7 containing ethanol (2% v/v). The insert shows the decay profile recorded at 540 nm.

Table 2. Properties of the ketyl radicals in neutral aqueous solution

compound	ε_{540} /dm^3 mol^{-1} cm^{-1}	$k_d/10^8$ dm^3 mol^{-1} s^{-1}
1	4500	4.8
2	3215	6.4
3	4050	2.8
4	3660	3.9

Flash photolysis studies showed that the triplet quenching reaction results in formation of the ketyl radical. This species has a characteristic[3,4] absorption spectrum (fig. 2). The same species can be generated by pulse-radiolytic reduction of the ketone in aqueous solution:

$$\begin{gathered} Ph_2CO^* + CH_3CH_2OH \rightarrow Ph_2COH + CH_3CHOH \\ Ph_2CO + e_{aq} \rightarrow Ph_2CO^- \\ Ph_2CO^- + H^+ \rightleftharpoons Ph_2COH. \end{gathered} \tag{1}$$

In the pulse radiolysis experiments at pH 7, it was found that whilst the hydrated electron reduced the ketone at a very fast rate ($k > 10^{10}$ dm^3 mol^{-1} s^{-1}), the 1-methyl-1-hydroxyethyl radical reacted too slowly to give an appreciable yield of ketyl radical. Under all conditions the ketyl radicals decayed by second-order kinetics. From measurements made at 540 nm and using the molar extinction coefficients given in

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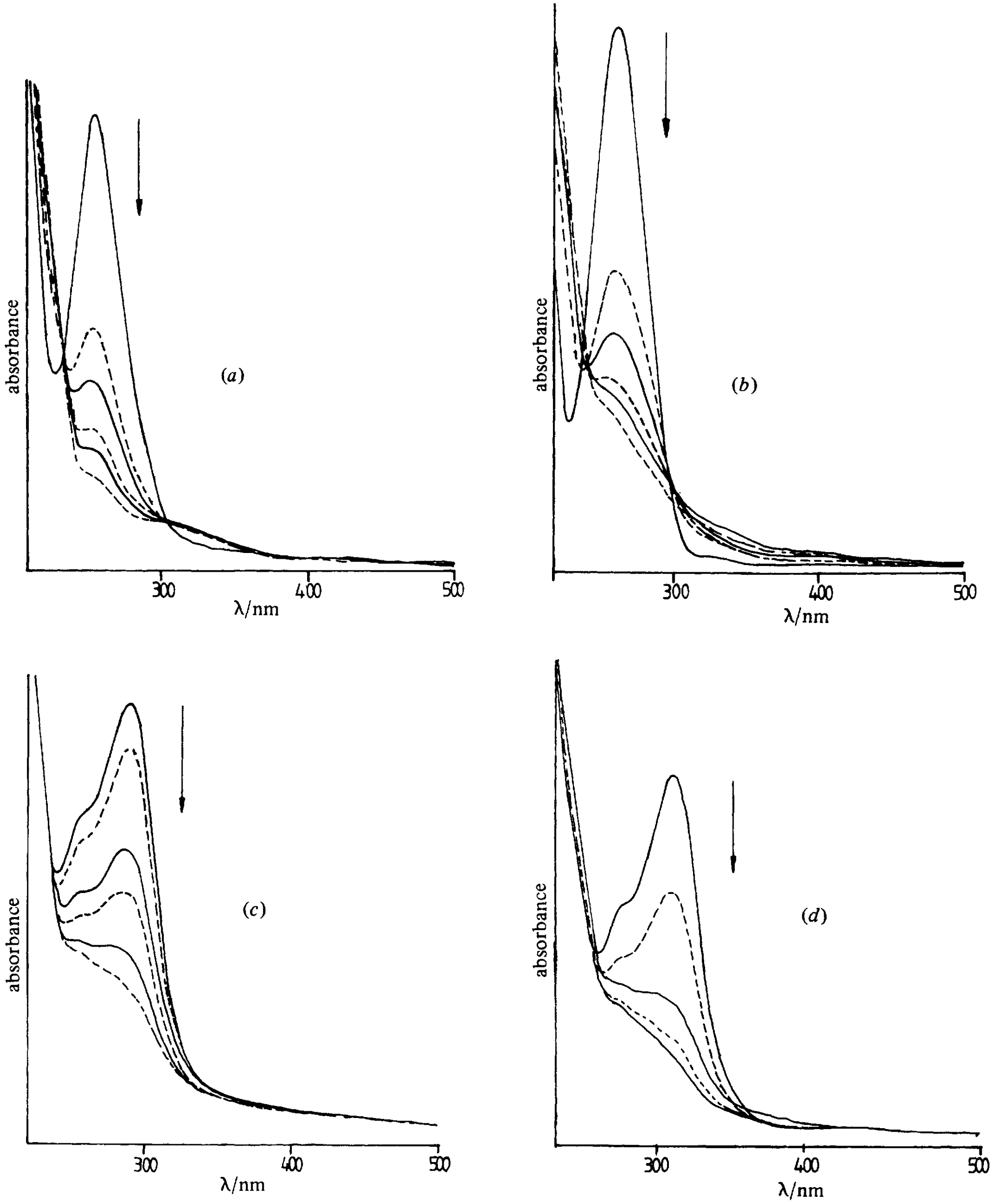

Fig. 3. Absorption spectra showing reduction of the various benzophenones upon photolysis in aqueous solution at pH 4.7 containing ethanol (2% v/v); (*a*) **1**, (*b*) **2**, (*c*) **3** and (*d*) **4**.

table 2, bimolecular rate constants for dimerisation of the ketyl radicals (k_d) were derived:

$$2Ph_2COH \xrightarrow{k_d} Ph_2C(OH)C(OH)Ph_2.$$

The observed rate constants show a small dependence upon the nature of the water-solubilising group. Taking into account the electrostatic repulsion between the radicals,

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Table 3. Efficiency of consumption of benzophenone upon irradiation (λ = 300 nm) in N_2-purged aqueous solution at pH 4.7 containing 2% v/v ethanol

compound	relative rate /mol dm^{-3} min^{-1}	ϕ
1	33.0	0.705
2	4.5	0.295
3	20.1	0.370
4	2.0	0.195

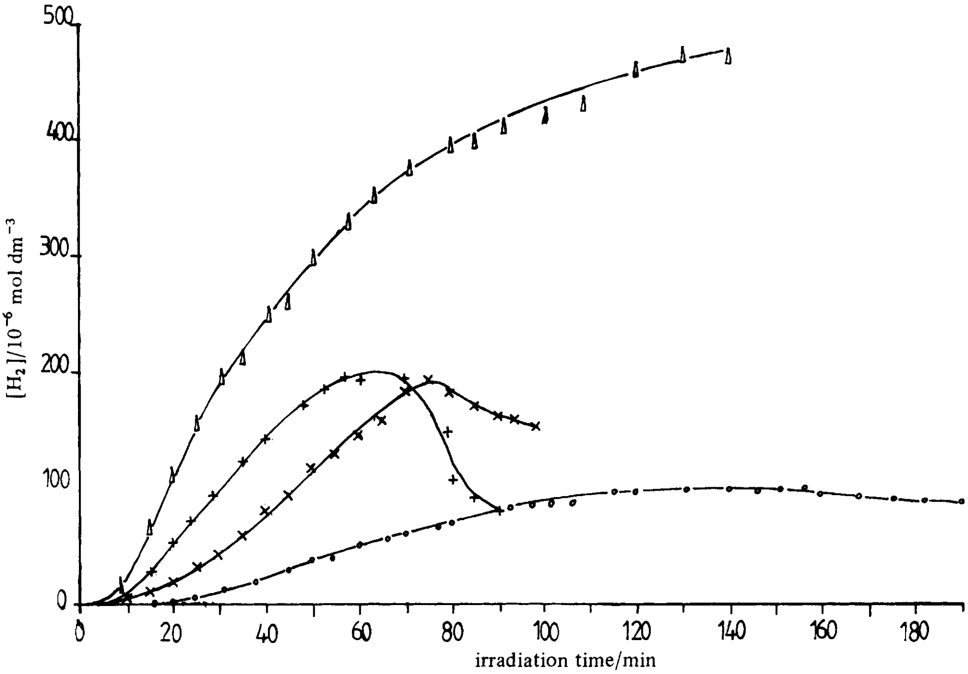

Fig. 4. Yield of H_2 evolved on photolysis of the benzophenones (5×10^{-4} mol dm^{-3}) in aqueous solution at pH 4.7 containing ethanol (2% v/v) and colloidal Pt (2×10^{-4} mol dm^{-3}): ×, **1**; △, **2**; +, **3**; ○, **4**.

the observed k_d values are fairly close to the diffusion-controlled limit. Indeed, for neutral benzophenone ketyl radicals $k_d = 1.7\times10^9$ dm^3 mol^{-1} s^{-1}.

As shown by eqn (1), the ketyl radicals have a pK transition due to deprotonation of the hydroxyl group. For benzophenone, flash photolysis[3] and pulse radiolysis[4] studies have found the pK to be 9.2 and we would expect the water-soluble derivatives to exhibit similar values. It should be noted that the deprotonated form (*i.e.* the ketone radical anion) decays much more slowly than the ketyl radical.

Steady-state Photolysis

All the compounds are fairly stable towards prolonged steady-state irradiation in N_2-purged aqueous solution at pH 4.7. There is some loss of the compounds under such

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conditions, especially **3** and **4**, where hydrogen abstraction from the sidechain can occur. Addition of ethanol to the solution results in a considerable enhancement in the rate of consumption of the ketone. This effect is shown in fig. 3, where the various compounds are irradiated in water containing ethanol (2% v/v). It is seen that the characteristic absorption band due to the ketone π,π^* transition is bleached upon irradiation.

$$2Ph_2CO^* + CH_3CH_2OH \rightarrow Ph_2C(OH)C(OH)Ph_2 + CH_3CHO.$$

The relative rates of reaction, as measured by following the absorption bleaching at *ca.* 280 nm, are collected in table 3. They are seen to depend markedly on the nature of the water-solubilising group. Quite clearly, negatively charged compounds react much more slowly than their positively charged analogues.

Similarly, the quantum yields for consumption of chromophore (table 3) are lower for the negatively charged compounds than for the positively charged benzophenones. With only 2% v/v ethanol there is incomplete quenching of the triplet excited state by the alcohol, especially for compounds **3** and **4**, where the triplet lifetime is short. Even so, under the experimental conditions the major reaction pathway for triplet excited benzophenone involves hydrogen abstraction from an ethanol molecule. The formation of acetaldehyde was confirmed in each case.

Hydrogen Formation

Irradiation of the above mixture in the presence of colloidal Pt inhibits pinacol formation.[7] During the irradiation acetaldehyde and H_2 are formed, as expected from the dehydrogenation of ethanol. However, loss of benzophenone does occur and upon prolonged irradiation the chromophoric group is extensively bleached. Fig. 4 shows the rates of H_2 formation on irradiation of compounds **1**–**4** (5×10^{-4} mol dm^{-3}) in water (pH 4.7) containing 2% v/v ethanol and colloidal Pt (2×10^{-4} mol dm^{-3}). In general, there is a short induction period before H_2 formation begins, which is most probably due to charging of the catalyst and removal of traces of O_2. The rate of H_2 formation then increases until a maximum value is reached.

Both the rate and total yield of H_2 formation depend on the nature of the water solubilising group. Interestingly, it is seen that the rate of H_2 formation does not parallel the rate of pinacol formation. Fig. 4 shows that compound **2** is by far the best as regards rate and total yield of H_2 production. The two positively charged compounds give high rates of H_2 production, but only for short irradiation times. For all three compounds, cessation of H_2 formation corresponds to complete loss of the benzophenone. In contrast, **4** evolves H_2 at a slow rate, but it remains stable under the operating conditions.

For compound **1**, the rate and total yield of H_2 formation were measured under a variety of experimental conditions. The efficiency of H_2 formation depended on the concentration of colloidal Pt, the amount of ethanol initially present in the system and the solution pH (fig. 5). In the absence of either Pt or ethanol, no H_2 is formed. The rate of H_2 formation increases linearly with concentration of both Pt and ethanol until a plateau is reached. Limiting values of H_2 evolution are found with Pt and ethanol concentrations of 3×10^{-4} mol dm^{-3} and 2% v/v, respectively. At pH < 8 the rate of H_2 production is practically independent of pH, but it increases markedly at higher pH. This effect appears to be connected with the pK of the ketyl radical. Since the ketone radical anion is considerably more stable than the corresponding ketyl radical, at least part of the effect is due to the inhibition of pinacol formation at higher pH. As shown by the data given in fig. 5, the quantum yield for formation of H_2 approaches unity at pH 11.5.

Table 4 gives rates and quantum yields for H_2 formation measured at pH 4.7 for the other compounds. Over short irradiations, the quantum yields are mostly high; the

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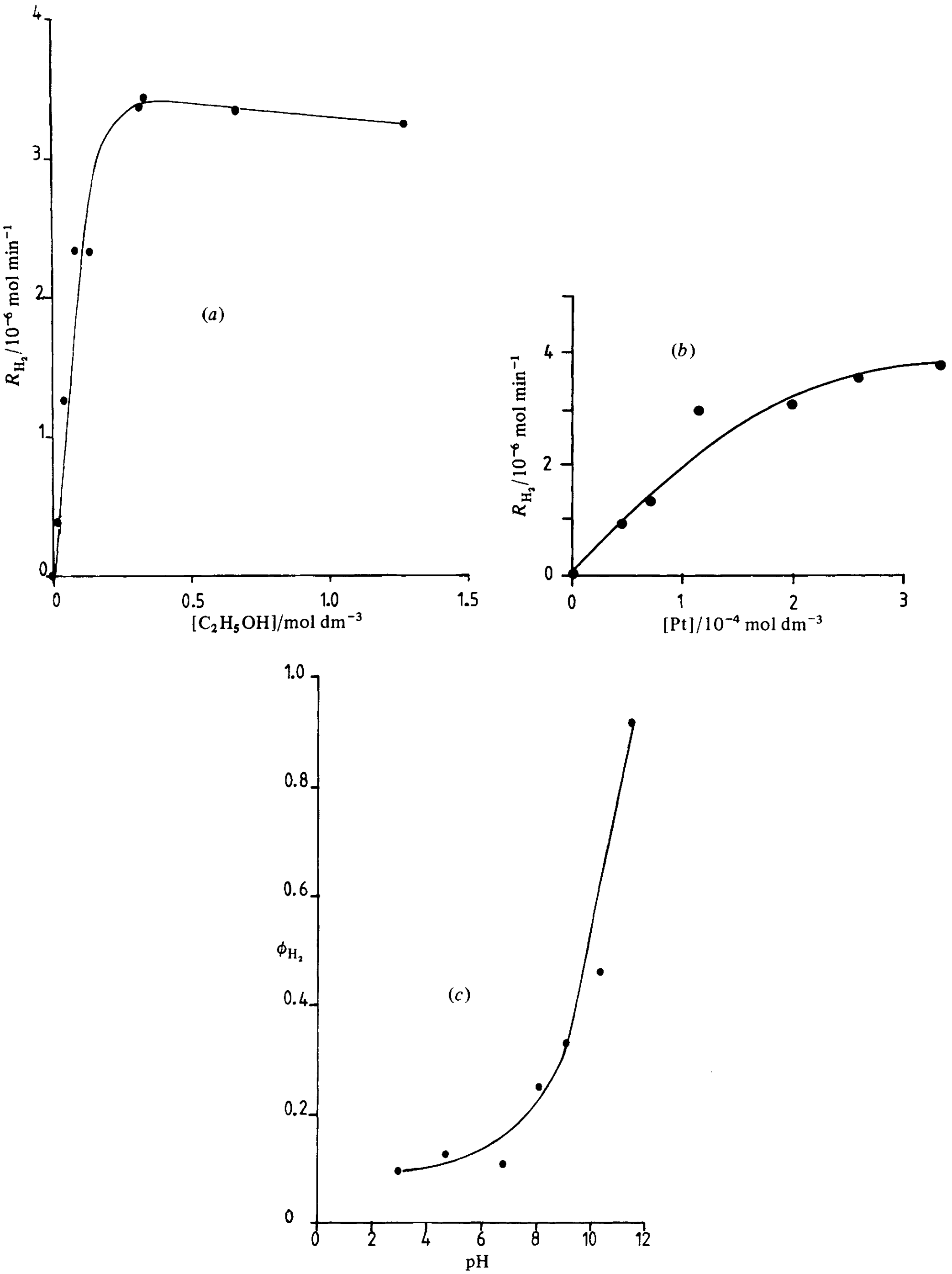

Fig. 5. Optimisation of H_2 evolution from photolysis of **1** in water. Plots (*a*) and (*b*) show the rate of H_2 evolution as a function of the concentrations of ethanol and Pt, respectively, at pH 4.7 and (*c*) shows the effect of pH on the initial quantum yield for H_2 formation. Unless otherwise stated, the reaction solution contained **1** (5×10^{-4} mol dm^{-3}), ethanol (2% v/v) and colloidal Pt (2×10^{-4} mol dm^{-3}).

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Table 4. Efficiency of hydrogen formation on irradiation of the benzophenones in water containing 2% v/v ethanol and colloidal Pt (2×10^{-4} mol dm^{-3})

compound	ϕ_{H_2}	R_{H_2}	turnover	ethanol (%)
1	0.131	3.51	43	6.5
2	0.281	7.50	107	16.2
3	0.170	4.54	43	6.5
4	0.041	1.09	21	3.2

Table 5. Electrochemical properties of the various benzophenones in N_2-purged aqueous solution containing KCl (0.2 mol dm^{-3})

compound	$D/10^{-6}$ cm^2 s^{-1}	pK	E_p^7	E_p^0	$E_{1/2}^7$
			V *vs.* SCE		
1	7.6	9.0	−1.21	−0.86	−1.19
2	8.8	9.7	−1.42	−1.02	−1.40
3	7.2	9.4	−1.39	−0.97	−1.37
4	7.7	9.5	−1.42	−1.01	−1.40

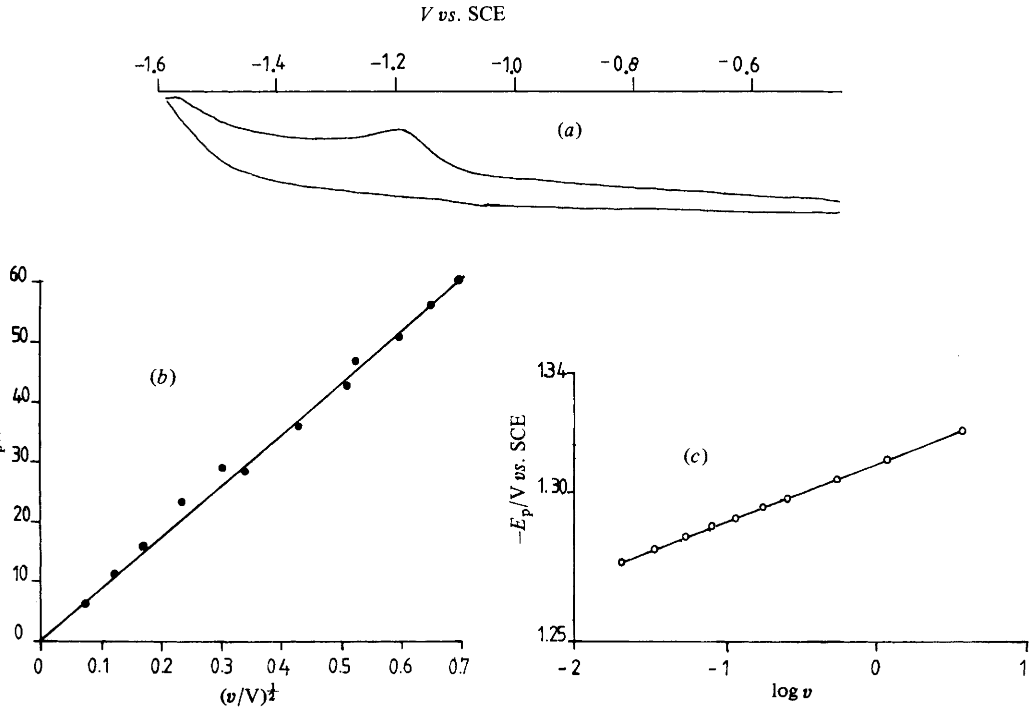

Fig. 6. Cyclic voltammetric parameters observed for reduction of **1** in neutral KCl solution: (*a*) a typical cyclic voltammogram, (*b*) the relationship between peak current and square root of voltage scan rate and (*c*) dependence of peak potential upon log of the voltage scan rate.

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values found for compounds **1** and **2** correspond to turnover numbers with respect to the benzophenone of 43 and 107, respectively. With 2% v/v ethanol, the final H_2 yields correspond to 6 and 17% conversion of ethanol for **1** and **2**, respectively. For **1** at pH 11.5 some 30% of the ethanol is consumed and the turnover number is 195.

Upon completion of exhaustive irradiations, it was found that removal of the evolved H_2 or addition of more Pt or ethanol did not restore the H_2-evolving capacity of the system. This confirms that the reason for the cessation of H_2 evolution is loss of the benzophenone. In blank experiments, it was found that stirring the benzophenones in aqueous solution containing colloidal Pt and H_2 did not reduce the ketones. However, under operating conditions it is probable that the surface of the catalyst is loaded with highly reactive hydrogen atoms. This suggests that the loaded catalyst reduces benzophenone to the alcohol during the latter stages of the reaction:[18]

$$Ph_2CO + 2H^{\cdot} \rightarrow Ph_2CHOH.$$

Cyclic Voltammetry

The water-soluble benzophenones were found to undergo an irreversible one-electron reduction process at a glassy carbon electrode in N_2-purged aqueous solution. Sharp, well defined peaks (half-widths *ca.* 40 mV) were seen on cathodic scans, but in no case could a peak be resolved on the reverse anodic scan (fig. 6). The peak profile did not depend on pH throughout the range $2 < \text{pH} < 12$, but the peak potential (E_p) was found to depend on both the solution pH and the voltage scan rate (v). As shown by fig. 6, the peak current (i_p) was a linear function of $v^{1/2}$, showing that the electrode process is diffusion-controlled. In fact, the peak current could be fitted to the equation[19]

$$i_p = 0.446AC_0F^{3/2}(D/RT)^{1/2}v^{1/2}$$

where A is the electrode surface area, C_0 is the initial concentration of benzophenone, and D is the diffusion coefficient of the compound. From such plots at pH 7, values for the diffusion coefficients were calculated (table 5).

The effect of pH on the peak potential is shown in fig. 7. At pH < 8, E_p decreases by *ca.* 59 mV for each unit increase in pH, whilst at pH > 8 deviations from linearity are seen and the slopes decrease. The observed results can be interpreted in terms of the equation[20]

$$E_p = E_p^0 + 0.05\log(K + [H^+])$$

where K refers to the dissociation constant of the ketyl radical and E_p^0 is the peak potential extrapolated to zero pH. By using the above equation, pK values for the various ketyl radicals were calculated (table 5). All the pK values lie around 9.5 ± 0.5 and are similar to that derived earlier[3, 4] for benzophenone in water (p$K = 9.2$). Also given in table 5 are the various E_p values measured at pH 7 and extrapolated to pH 0. Comparison of these values shows that the nature of the water-solubilising group has only a modest effect upon the redox potentials and pKs. Both sets of values depend on the relative amount of electron density residing upon the carbonyl group. It is seen that the sulphonic acid group in compound **2**, and to a much lesser extent in **4**, raises the electron density on the aromatic nucleus, giving a higher pK for the ketyl radical and a lower E_p.

The irreversibility of the cyclic voltammograms is due to rapid dimerisation of the ketyl radicals.[21] At pH < 8 the form of fig. 7 shows that a single proton accompanies the one-electron reduction of the compound. Above the pK, the reduced compound decays *via*

$$Ph_2COH + Ph_2CO^- \rightarrow Ph_2C(OH)C(O^-)Ph_2$$

$$Ph_2C(OH)C(O^-)Ph_2 + H^+ \rightarrow Ph_2C(OH)C(OH)Ph_2$$

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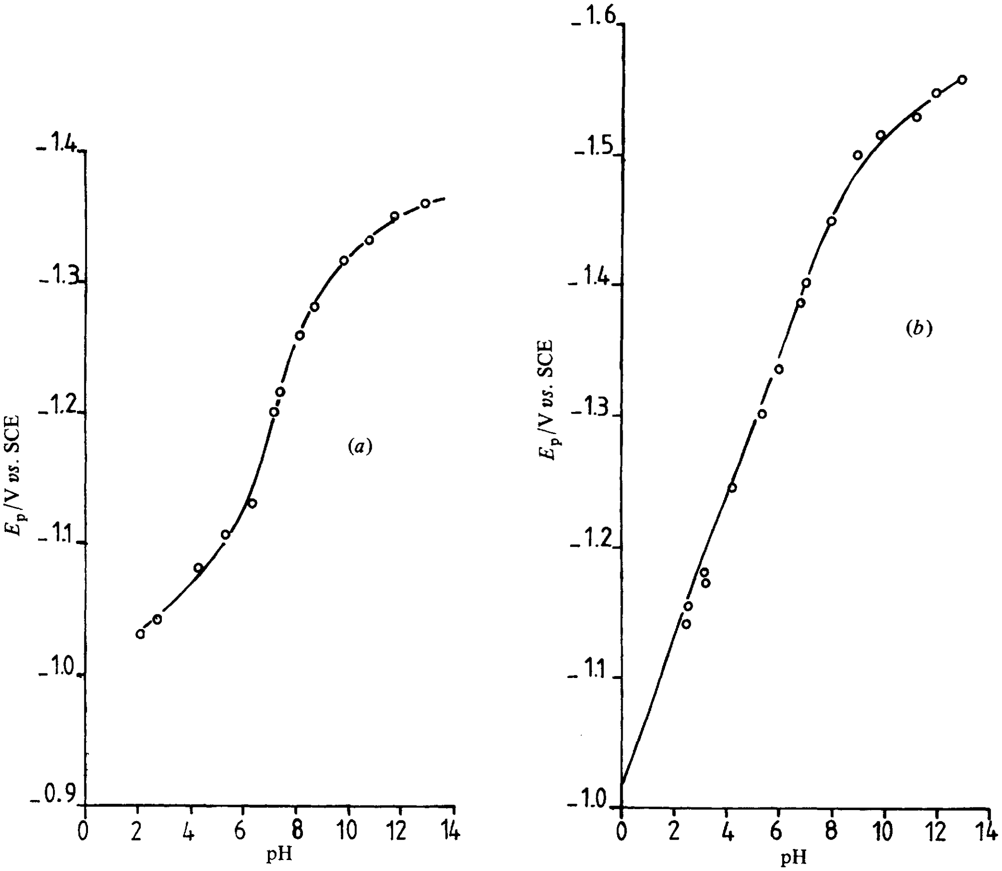

Fig. 7 (*a*) and (*b*). For caption see opposite.

for which E_p should decrease by 40 mV for each unit increase in pH. Because of this irreversible nature of the electrochemistry it is not easy to convert the observed E_p values into redox potentials. It was found that at pH 7 the actual peak potentials depended upon the voltage scan rate according to:[22]

$$E_p = E_{1/2} - 0.902(RT/3F) + (RT/3F)\ln(2a/3)$$

where $a = (RT/Fv\,C_0 k_d)$.

In all cases, plots of E_p *vs.* $\log v$ were linear (fig. 6) with slopes of *ca.* 20 mV per pH unit, and allowed calculation of the half-wave potential for one-electron reduction of the compounds at pH 7 (table 5). All the ketyl radicals should reduce water to H_2 at pH 7.

Mechanism of the H_2-evolving Process

The above experiments[7] have shown that colloidal Pt particles are able to intercept dimerisation of the ketyl radicals and mediate H_2 formation. From electrochemical measurements, it appears that both the ketyl radical derived from the benzophenone and the 1-hydroxyethyl radical[23] derived from ethanol have sufficient reducing power to cause reduction of water under the experimental conditions. It has been shown that the

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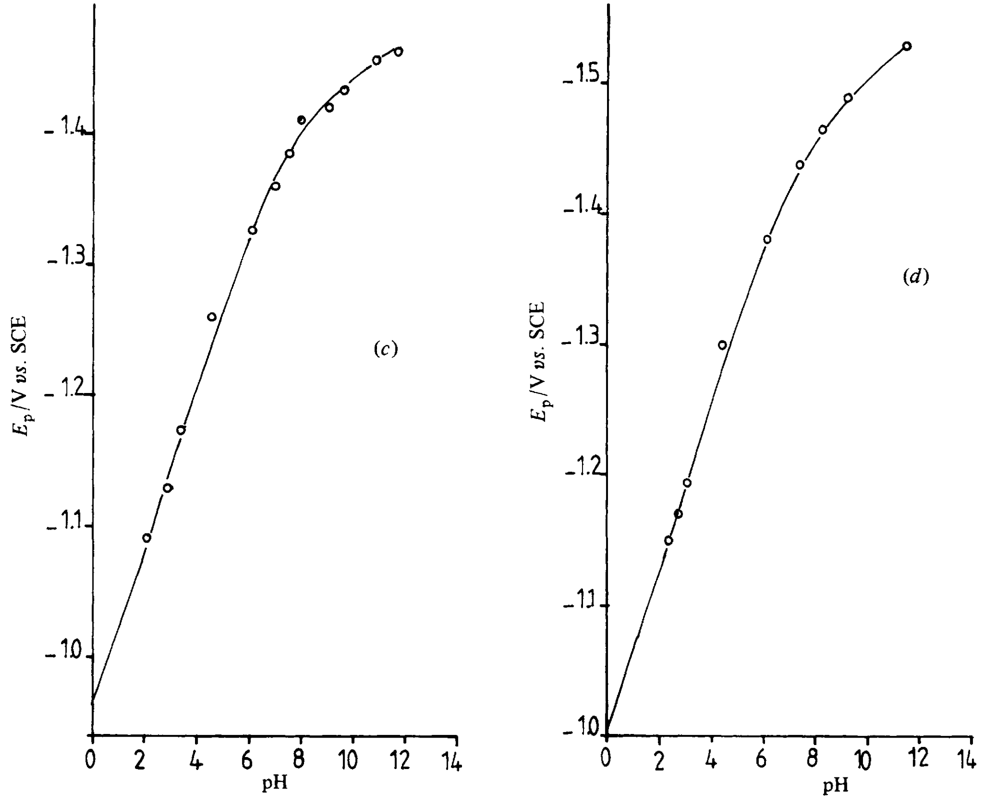

Fig. 7. Effect of pH upon the peak potential for reduction of the various benzophenones in aqueous KCl solution: (*a*) **1**, (*b*) **2**, (*c*) **3** and (*d*) **4**.

reducing radicals derived by hydrogen abstraction from alcohols will transfer electrons to colloidal particles of noble metals.[24] This infers that at least part of the evolved H_2 is due to reduction of water on the catalyst surface by the 1-hydroxyethyl radicals:

$$2CH_3CHOH \rightarrow 2CH_3CHO + H_2.$$

The redox potential[23] for this radical is *ca.* -1.18 and -1.83 V *vs.* NHE at pH 7 and 12, respectively. In view of the large thermodynamic driving force for water reduction at all pH values, it seems likely that interaction between the colloidal Pt particles and 1-hydroxyethyl radicals will be diffusion-controlled.

Pulse radiolysis experiments were carried out to determine if the ketyl radicals could also serve as reducing species for water. Hydrated electrons formed upon radiolysis of N_2-saturated water containing 5% v/v propan-2-ol were used to reduce the benzophenones. Decay of the intermediate ketyl radicals was monitored at 540 nm; in the absence of colloidal Pt the decay was second-order. With concentrations of colloidal Pt higher than 5×10^{-5} mol dm^{-3}, decay of the ketyl radicals could be analysed in terms of a pseudo-first-order process. The derived first-order rate constant increased with increasing concentration of colloidal Pt (fig. 8), giving rise to the bimolecular rate constant for interaction between the reactants (k_{Pt}). This second-order rate constant was found to be markedly dependent upon the actual benzophenone used (table 6). Quite clearly, positively charged compounds react at much higher rates than do negatively charged derivatives. This can be attributed to electrostatic effects since the colloid retains

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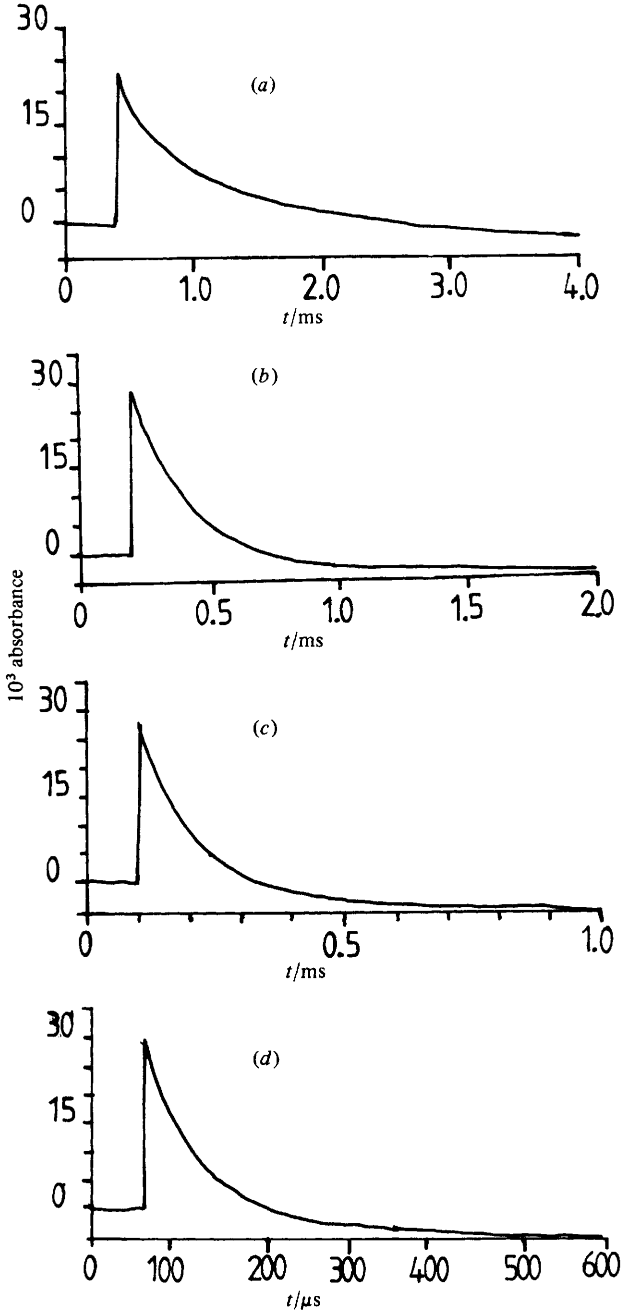

Fig. 8 (*a*)–(*d*). For caption see opposite.

a definite negative charge at pH > 3. Thus, the ketyl radicals derived from **1** and **3** are attracted to the Pt surface where they can deposit their extra electron. Ketyl radicals derived from **2** and **4** are repelled from the catalyst surface so that the rate of electron transfer to the colloid is relatively slow.

Once charged, the Pt colloid reduces water to H_2, although it has been suggested that some of the reducing equivalents are retained in the form of surface-bound hydrogen

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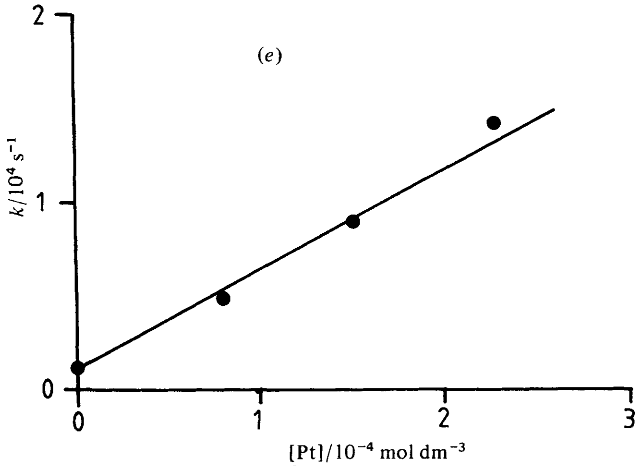

Fig. 8. Effect of colloidal Pt on the rate of decay of the ketyl radical derived from **1** in neutral aqueous solution: (Pt) = (*a*) 0, (*b*) 0.82×10^{-4}, (*c*) 1.52×10^{-4} and (*d*) 2.26×10^{-4} mol dm^{-3}. (*e*) shows the derived pseudo-first-order rate constant as a function of the Pt concentration.

Table 6. Kinetic parameters for the interaction of the various ketyl radicals with colloidal Pt particles in water at pH 7

compound	$t_{1/2}$ /μs	$k_{Pt}/10^6$ $dm^3\ mol^{-1}\ s^{-1}$
1	85	52.7
2	1250	3.0
3	62	71.5
4	1050	4.0

atoms.[25] Such species are highly reactive towards hydrogenation of unsaturated bonds and, presumably, they are responsible for the observed reduction of the benzophenones.[18] In this respect it should be noted that compounds **1** and **3** are more susceptible towards reduction since they are electrostatically attracted to the colloid surface.

For compounds **1** and **3** the measured k_{Pt} values are essentially identical. In these experiments, the presence of 2×10^{-4} mol dm^{-3} colloidal Pt is sufficient to decrease the half-life of the ketyl radical from *ca.* 1 ms to < 100 μs. This means that the Pt particles can intercept the ketyl radicals before any significant dimerisation occurs. For the negatively charged compounds, much higher concentrations of colloidal Pt are needed to ensure that all the ketyl radicals are trapped by the catalyst. Under pulse radiolysis conditions, 2×10^{-4} mol dm^{-3} colloidal Pt traps *ca.* 25% of the ketyl radicals obtained from **2**, whereas the trapping is 100% effective for **1** and **3**. This shows the importance of electrostatic factors in these experiments, but it must be noted that the high initial concentration of ketyl radicals produced in the pulse radiolysis experiments favours the second-order dimerisation reaction.Under steady-state conditions, a higher fraction of the negatively charged ketyl radicals will be trapped by the same concentration of Pt colloid.

The Pt catalyst used in these experiments has a particle radius of 1.0 nm, as determined by high-resolution electron microscopy. This means that there are on average 280 Pt atoms clustered into one particle. Taking this factor into account, the

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bimolecular rate constant for interaction between Pt particles and ketyl radicals derived from **1** becomes 1.4×10^{10} $dm^3\ mol^{-1}\ s^{-1}$, which must be close to the diffusion-controlled limit.

From steady-state photochemical experiments it is clear that during the early stages of the reaction collision between ketyl radicals and colloidal Pt does not lead to destruction of the benzophenone.[7] This suggests that the reaction involves electron transfer to the colloid and subsequent discharge through reduction of surface-bound protons:

$$2Ph_2COH \rightarrow 2Ph_2CO + H_2.$$

Thus, the overall reaction corresponds to the dehydrogenation of ethanol. As the reaction proceeds, colloid particles loaded with surface bound hydrogen atoms begin to catalyse reduction of the benzophenone. This side-reaction, which is restricted by using a negatively charged compound, short-circuits the cyclic nature of the system. Its occurrence means that the quantum yield for H_2 formation decreases during the irradiation from an initial value that is close to the quantum yield for formation of pinacol in the absence of Pt to zero.

Conclusions

This work shows that benzophenone derivatives can photodehydrogenate ethanol in dilute aqueous solution with high efficiency. Low concentrations of ethanol and colloidal Pt provide satisfactory experimental conditions, and by careful optimisation the quantum yield for H_2 formation can approach unity. Reasonable turnover numbers are obtained, showing that the benzophenone functions as a catalyst for the system, and the reaction proceeds with high rate under ambient conditions. The process results in net storage of energy. Unfortunately, u.v. light is required to drive the reaction and the overall conversion efficiency with respect to sunlight is small. This problem can be partially solved by organic synthesis, provided water-soluble, coloured materials can be prepared that possess lowest-energy excited states having n,π^* character.

It should be noted that the overall efficiency of the photosystem is controlled by the nature of the ionic substituent used to induce solubility in water. This is due to electrostatic interactions involved in the reaction between intermediate ketyl radicals and Pt colloid. It is possible that the reaction efficiency could be improved by varying the position and nature of the substituent.

We have concentrated here on the photogeneration of H_2, but the photosystems could be developed to drive certain synthetic reactions. Thus, the formation of water-soluble pinacols (by dimerisation of the ketyl radicals) and alcohols (by catalysed reduction of the ketone) can be considered. Performing the reaction in the presence of ammonia should result in formation of a primary amine. Furthermore, replacing the alcohol with an alkylamine or sulphide permits synthesis of a wide variety of potentially novel compounds.

We thank the S.E.R.C. and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support of this work. The donation of water-soluble benzophenones by Ward Blenkinsop Co. Ltd is gratefully acknowledged.

References

1 J. N. Pitts and J. G. Calvert, *Photochemistry* (J. Wiley, New York, 1966).
2 G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 1961, **57**, 1686.
3 A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2038; 2051.
4 G. E. Adams and R. L. Willson, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 719; E. Hayon, T. Ibata, N. N. Lichtin and M. Simic, *J. Phys. Chem.*, 1972, **76**, 2076.
5 L. Nadjo and J. M. Saveant, *J. Electroanal. Chem.*, 1971, **33**, 419.

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Published on 01 January 1988. Downloaded by University of Michigan Library on 30/10/2014 02:21:39.

6 M. Simic, P. Neta and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794.
7 C. K. Gratzel and M. Gratzel, *J. Am. Chem. Soc.*, 1979, **101**, 7741.
8 A. Bonamy, J. P. Fouassier, D. J. Lougnot and P. N. Green, *J. Polym. Sci., Polym. Lett. Ed.*, 1982, **20**, 315.
9 D. J. Lougnot, P. Jacques, J. P. Fouassier, H. L. Casal, K. T. Nguyen and J. C. Scaiano, *Can. J. Chem.*, 1985, **63**, 3001.
10 G. C. Bond, *Trans. Faraday Soc.*, 1956, **52**, 1235.
11 D. A. Jefferson, J. M. Thomas, G. R. Milward, K. Tsuno, A. Harriman and R. D. Brydson, *Nature (London)*, 1986, **323**, 428.
12 S. J. Valenty, *Anal. Chem.*, 1978, **50**, 669.
13 W. D. K. Clark, A. D. Litt and C. Steel, *J. Am. Chem. Soc.*, 1969, **91**, 5413.
14 G. Porter and P. Suppan, *Trans. Faraday Soc.*, 1965, **61**, 512.
15 J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, 1963, **85**, 528.
16 M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 539.
17 C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, 1969, **65**, 2823.
18 E. K. Rideal, *J. Am. Chem. Soc.*, 1920, **42**, 749.
19 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* (J. Wiley, New York, 1980).
20 S. V. Jovanovic, A. Harriman and M. Simic, *J. Phys. Chem.*, 1986, **90**, 1935.
21 M. I. Olmstead, R. G. Hamilton and R. S. Nicholson, *Anal. Chem.*, 1969, **41**, 260.
22 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
23 J. Lilie, G. Beck and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 1971, **75**, 458.
24 A. Henglein, *J. Phys. Chem.*, 1979, **83**, 2209; 2858.
25 J. M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (MacDonald Publ. Co., New York, 1970), vol. 2, chap. 10.

Paper 7/1537; *Received* 20*th August*, 1987