Photo-oxidation of Triarylmethanes sensitised by Carbonium Ions

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Absorption of light by stable carbonium ions (xanthydryl, triphenylmethyl, and 5H-dibenzo[a,d]cycloheptenyl cations) in solution in trifluoroacetic acid containing oxygen brings about oxidation of triarylmethanes to the corresponding triarylmethyl cation. Excess of molecular oxygen inhibits the photo-oxidation. The dependence of the quantum yield for photo-oxidation on the concentration of triarylmethane indicates that the hydrocarbon reacts directly with an excited state, believed to be triplet, of the sensitising cation. The effect of ring substituents in triphenylmethane on the partitioning of the triplet sensitiser between oxygen quenching and reaction with the hydrocarbon is interpreted as evidence that the photo-oxidation is initiated by electron transfer from triarylmethane to the excited sensitiser.

THE extensive literature of carbonium ion chemistry [1] is almost wholly devoted to the behaviour of carbonium ions in their ground states. Recently, however, a number of reports have been published of the reactions undergone by carbonium ions such as triphenylmethyl,[2] cycloheptatrienyl,[3] triphenylcyclopropenyl,[3] protonated durene,[4] and eucarvone [5] cations on photo-excitation. Moreover, there is growing interest in the phenomenon of apparent acid catalysis of photochemical reactions [6] in which, for example, intermediate dipolar species or highly strained cyclic olefins [7] on protonation give rise to stable photo-products by way of carbonium ions. In this paper we report some of our observations on the photo-oxidation of triarylmethanes in which carbonium ions act as sensitisers since this throws further light on the nature and mechanism of reaction of excited states of these important intermediates.

RESULTS

In the course of kinetic studies on hydride transfer between substituted triphenylmethanes and fluorenyl cations in trifluoroacetic acid [8] it was noticed that, in certain cases, some conversion of the hydrocarbon into the corresponding triarylmethyl cation occurred before introduction of the hydride-ion acceptor into the reaction mixture. This oxidation was readily shown to be photochemical and the autocatalytic nature of the course of reaction suggested that the product carbonium ion was capable of sensitising further oxidation. This was confirmed by the observation that when carbonium ions (introduced into the reaction mixture as the alcohol) were present initially, there was no induction period. Further experiments showed that the reaction is general in acid media and is not associated specifically with the presence of trifluoroacetic acid. Accordingly a more detailed investigation was undertaken.

Three carbonium ions having quite different absorption spectra were used. These were xanthydryl (1), triphenylmethyl (2), and 5H-dibenzo[a,d]cycloheptenyl (3) cations. All are quantitatively formed on dissolution of the corresponding alcohol in trifluoroacetic acid. The stabilities

of these carbonium ions and their spectroscopic characteristics (absorption and fluorescence) in trifluoroacetic acid solution are recorded in Table 1.
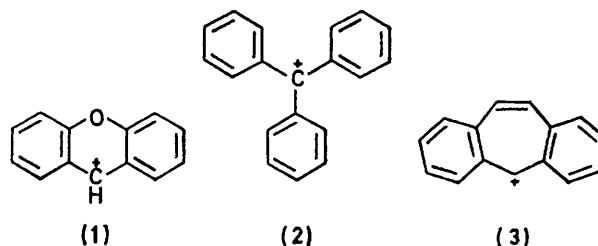

(1)   (2)   (3)

TABLE 1

Properties of sensitiser carbonium ions in trifluoroacetic acid

Sensitiser	pK_{R^+} [a]	Absorption spectrum		Fluorescence	
		$\lambda_{max.}/nm$	$\varepsilon_{max.}$	$\lambda_{max.}/nm$	λ [b]
(1)	−0·84	375	40,000	497	368
		425	5000		
(2)	−6·63	410	40,000	505	404
		425	39,000		436
(3)	−3·7 (−5·8)	370	12,000	554	868
		540	5000		

[a] Determined in aqueous sulphuric acid.[1]   [b] Wavelength used for sensitising photo-oxidation.

Irradiation at ca. 25 °C of dilute (ca. 2×10^{-5}M) solutions of the sensitiser cations in trifluoroacetic acid containing dissolved oxygen and triphenylmethane (10^{-5}—10^{-4}M) led to quantitative formation of triphenylmethyl cation. The appearance of the product carbonium ion was monitored spectrophotometrically. The light used to excite the sensitisers was selected from the output of a medium-pressure mercury arc by use of interference filters; the wavelengths used for each sensitiser are indicated in Table 1. 4-Substituted triphenylmethanes are oxidised in the same way as the parent hydrocarbon. In those cases where the product cation has a higher pK_{R^+} value than the sensitiser, control experiments established that thermal (i.e., ground-state) hydride transfer was too slow to complicate the photo-oxidation, at least in the range of concentrations employed

[1] See, e.g., D. Bethell and V. Gold, ' Carbonium Ions. An Introduction,' Academic Press, London and New York, 1967.

[2] (a) E. E. van Tamelen and T. M. Cole, J. Amer. Chem. Soc., 1970, 92, 4123; (b) 1971, 93, 6158; (c) T. M. Cole, ibid., 1970, 92, 4124; see also D. M. Allen and E. D. Owen, Chem. Comm., 1971, 848.

[3] E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, J. Amer. Chem. Soc., 1968, 90, 1372; E. E. van Tamelen, R. H. Greeley, and H. Schumacher, ibid., 1971, 93, 6151.

[4] R. F. Childs, M. Sakai, and S. Winstein, J. Amer. Chem. Soc., 1968, 90, 7144.

[5] K. E. Hine and R. F. Childs, J. Amer. Chem. Soc., 1971, 93, 2323; see also B. Parrington and R. F. Childs, Chem. Comm., 1970, 1581.

[6] See, e.g., D. Bryce-Smith, G. B. Cox, and A. Gilbert, Chem. Comm., 1971, 914, and succeeding papers.

[7] P. J. Kropp, J. Amer. Chem. Soc., 1969, 91, 5783.

[8] P. A. Kearney, Ph.D. Thesis, Liverpool, 1970.

in this investigation. No oxidation was observed in the dark and no detectable consumption of the sensitiser occurred during photo-oxidation of the triarylmethanes (*cf.* refs. 2 and 3).

The influence of light intensity on the initial rate of production of triphenylmethyl cation and its 4-phenyl analogue from the corresponding triarylmethane is illustrated by the results in Table 2. It can be seen that the rate of photo-oxidation is directly proportional to the light intensity.

TABLE 2

Influence of light intensity (λ 368 nm) on the initial rate of photo-oxidation of triarylmethanes sensitised by xanthydryl cation (2×10^{-5}M)

Triaryl-methane (Ar_3CH)	$10^5[Ar_3CH]/$ M	$10^{-16} \times$ Intensity (quanta s^{-1})	$10^8 d[Ar_3CH]/dt$ mol l^{-1} s^{-1}
Ph_3CH	2·0	1·07	2·42
		0·44	0·91
		0·29	0·68
4-$Ph\cdot C_6H_4CHPh_2$	2·0	1·07	38·8
		0·69	28·2
		0·59	23·6

Quantum yields (Φ; the subscript indicates the sensitiser used) for photo-oxidation were determined as a function of triarylmethane concentration and structure by conventional means.[9] The extent of conversion of triarylmethane into triarylmethyl cation was less than 8% in all cases. Tables 3 and 4 contain results showing the concentration-dependence of Φ for oxidation of 4-phenyl- and 4-methoxy-triphenylmethane respectively for different sensitisers and oxygen concentrations (saturation of the reaction mixture with air or pure oxygen). Table 5 gives similar results for reactions in which, during photolysis, the solution was continuously saturated with commercial ' oxygen-free ' nitrogen (5—10 p.p.m. oxygen). Table 6 shows the effect of 4-substituents in triphenylmethane on the quantum yield for photo-oxidation at a fixed hydrocarbon concentration using each of the three sensitiser carbonium ions. The presence of deuterium on the α-carbon atom of triphenylmethane and its 4-methoxy-analogue has little or no effect on the quantum yield.

TABLE 3

Quantum yields for photo-oxidation of 4-phenyltriphenylmethane sensitised by carbonium ions (1) and (2) in air-saturated trifluoroacetic acid

$10^5[Ar_3CH]/$M	1·0	1·5	2·0	3·0	4·0	9·2	18·4	37·0
$10^3\Phi_1$	3·20		5·70	8·75	10·2	36·4	57·0	73·0
$10^3\Phi_2$		0·75	0·99	1·30	1·54	2·34	4·80	7·00	9·40

TABLE 4

Quantum yields for photo-oxidation of 4-methoxytriphenylmethane sensitised by carbonium ions (1) and (3) in air-saturated trifluoroacetic acid

$10^5[Ar_3CH]/$M	1·0	1·5	2·0	3·0	4·0	6·0
$10^3\Phi_1$	2·08	2·47	3·90	5·05	7·00	11·0

$10^5[Ar_3CH]/$M	8·0	11·2	22·3	33·5	44·6
$10^3\Phi_1$	14·2	14·4	34·0	39·0	44·0

$10^5[Ar_3CH]/$M	1·0	2·0	3·0	4·0	10·0	20·0	30·0	40·0
$10^3\Phi_1$ [a]		1·02	1·60	2·18	4·95	13·8	22·8	24·0
$10^3\Phi_3$	0·75	1·35	1·45	2·52	5·10	10·2		21·4

[a] Oxygen-saturated trifluoroacetic acid.

A notable feature of the results in Tables 3—5 is the observation that, other things being equal, the more oxygen in the reaction mixture the lower the quantum yield. Thus the highest quantum yields for photo-oxidation are achieved

TABLE 5

Quantum yields for photo-oxidation of 4-substituted triphenylmethanes sensitised by carbonium ions (1), (2), and (3) in trifluoroacetic acid saturated with ' oxygen-free ' nitrogen (5—10 p.p.m. O_2)

Sensitiser	4-Substituent	$10^5[Ph_3CH]/$M	Φ
(1)	MeO	2·0	0·090
		4·0	0·100
		11·2	0·090
		44·6	0·100
(2)	Ph	4·0	0·0082
		20·0	0·0092
		40·0	0·0095
	MeO	2·0	0·0089 [a]
		4·0	0·0080 [a]
		20·0	0·0088 [a]
(3)	MeO	1·0	0·078
		2·0	0·090
		4·0	0·070
		10·0	0·078

[a] Sensitiser irradiated at 436 nm.

TABLE 6

The effect of 4-substituents on the quantum yield of photo-oxidation of triphenylmethane ($2 \cdot 0 \times 10^{-5}$M) sensitised by carbonium ions (1), (2), and (3) in air-saturated trifluoroacetic acid

4-Substituent	$10^3\Phi_1$	$10^3\Phi_2$	$10^3\Phi_3$
Ph	5·60	1·30	1·27
MeO	4·20 [a,b]	0·80 [b]	1·35
Bu^t	4·15	1·54	0·14
Me	3·35	1·10	0·087
Cl	0·40	1·60	0·165
H	0·26 [c]	1·87 [c]	0·038
NO_2	0·17	1·15	0·030

[a] 4,4'-Dimethoxytriphenylmethane, $\Phi_1 = 4·94 \times 10^{-3}$. 4,4',4''-Trimethoxytriphenylmethane, $\Phi_1 = 5·12 \times 10^{-3}$. [b] α-Deuterio-4-methoxytriphenylmethane, $\Phi_1 = 3·09 \times 10^{-3}$, $\Phi_2 = 0·80 \times 10^{-3}$. [c] α-Deuteriotriphenylmethane, $\Phi_1 = 0·26 \times 10^{-3}$, $\Phi_2 = 1·87 \times 10^{-3}$.

under *nominally* oxygen-free conditions. Careful purification of nitrogen by passage through Fieser's solution stops photo-oxidation. Clearly, molecular oxygen in excess of the amount stoicheiometrically necessary for the reaction inhibits photo-oxidation.

At a fixed oxygen concentration, Φ^{-1} is a linear function of the reciprocal of the concentration of triarylmethane. Representative plots of Φ^{-1} against $[Ar_3CH]^{-1}$ are shown in Figure 1. The form of these plots is that expected for partitioning of a photochemically generated reactive intermediate between quenching and product, in this case carbonium ion, formation. The plots in Figure 1 demonstrate clearly the quenching of photo-oxidation by excess of molecular oxygen. They also indicate that the intercept of the plots of Φ^{-1} against $[Ar_3CH]^{-1}$ is determined only by the nature of the sensitising cation and not by the nature of the triarylmethane undergoing oxidation, nor by the oxygen concentration in the system. On the other hand, the gradients of the lines in Figure 1 are determined by all these reaction variables. Of particular importance

[9] J. Calvert and J. N. Pitts, ' Photochemistry,' Wiley, New York, 1966, ch. 7.

is the observation that the gradient is proportional to the oxygen concentration: thus use of ' oxygen-free ' nitrogen to saturate reaction mixtures gives values of Φ which are, within the experimental uncertainty, invariant with triphenylmethane concentration and equal to the value derived from the intercept of the plots of Φ^{-1} against $[Ar_3CH]^{-1}$ at $[Ar_3CH]^{-1} = 0$ for the same sensitiser.
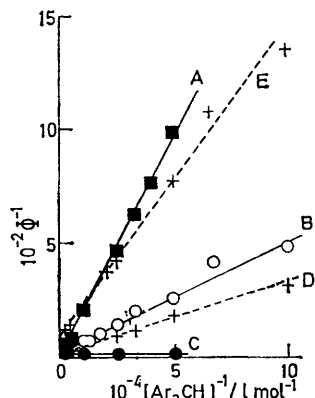

FIGURE 1 Dependence of quantum yield on concentration of 4-substituted triphenylmethane, Ar_3CH, under various conditions; A, 4-substituent, MeO; sensitiser (1); saturating gas, oxygen; B, MeO, (1), air; C, MeO, (1), nitrogen containing 5—10 p.p.m. oxygen; D, Ph, (1), air; E, Ph, (2), air

The fluorescence of the sensitising cations was not observed to be quenched by added triarylmethanes and that for triphenylmethyl cation is known [2a] to be unaffected when oxygen is present. Thus oxygen quenching of photo-oxidation of triarylmethanes is to be associated with quenching of an excited *triplet* state of the sensitiser. The rules of spin conservation require that such a process give rise to

reduces this substantially without decreasing the acidity of the medium below the level at which triphenylmethanol is completely converted into triphenylmethyl cation. Irradiation ($\lambda > 300$ nm) of a solution of tetracyclone and triphenylmethyl cation in air-saturated acetic acid–trifluoroacetic acid (1 : 1 v/v) did indeed give rise to detectable amounts of *cis*-dibenzoylstilbene. However, when the carbonium ion was selectively excited by use of an interference filter none was formed, although the tetracyclone, stable in the absence of the carbonium ion or light, was quite rapidly consumed.[*] Methylene Blue when irradiated in an air-saturated acetic–trifluoroacetic acid mixture did not bring about oxidation of triphenylmethane to triphenylmethyl cation. Thus we can offer no direct evidence for the formation of singlet molecular oxygen in these reactions, and the mechanism of oxygen quenching of carbonium ion-sensitised photo-oxidations must remain open.

Besides molecular oxygen, quenching of photo-oxidation by other species has been investigated. The compounds examined were anisole, hexamethylbenzene, and fluorenone, and the results are summarised in Table 7, together with ionisation potentials and energies of the lowest triplet state of these quenchers.[11-13]

Under the conditions of the quenching experiments (Table 7) the most effective quencher of photo-oxidation, hexamethylbenzene, had little effect ($<2\%$) on the intensity of fluorescence of xanthydryl and triphenylmethyl cations, strongly suggesting that it interacts mainly with the triplet state of the sensitisers. This conclusion is supported by the following results from irradiations carried out in the cavity of an e.s.r. spectrometer.

Continuous irradiation ($\lambda > 300$ nm) of a frozen solution of triphenylmethyl cation (10^{-3}M) in trifluoroacetic acid which had been freed from most of its oxygen by bubbling with nitrogen gave a broad e.s.r. signal centred at *ca.* $g = 2$. An identical signal (Figure 2,A) was observed when the

TABLE 7

Quenching of photo-oxidation of 4-substituted triphenylmethanes sensitised by xanthydryl cation in air-saturated trifluoroacetic acid

Quencher Q	$10^3[Q]/M$	4-Substnt.	$10^5[Ar_3CH]/M$	Φ_Q/Φ	I.P.[11]/ev	E_T[12]/kcal mol^{-1}
Anisole	10	Bu^t	2·0	Very small	8·22	80·3
Hexamethylbenzene	1·0	Ph	2·0	0	7·82	*ca.* 78 [a]
	1·0	H	2·0	0 [b]		
Fluorenone	2·0	Ph	2·0	0·35 [b]	≮9·45 [d]	53·3

[a] Ref. 13. [b] Sensitiser: triphenylmethyl cation. [c] 1 : 1 (v/v) acetic : trifluoroacetic acid. [d] Value for benzophenone.

two singlet species and efforts have been made to detect singlet molecular oxygen in these systems by trapping experiments.

Many well-established traps for singlet oxygen such as 2,5-dimethylfuran and tetramethylethylene are useless in trifluoroacetic acid solution because of competing acid-induced reactions. Tetraphenylcyclopentadienone (' tetracyclone ') is reported to add singlet molecular oxygen giving, after loss of carbon monoxide from the initial adduct, *cis*-dibenzoylstilbene.[10] While tetracyclone is reversibly protonated in pure trifluoroacetic acid (as indicated by the decreased absorbance at 505 nm), dilution with acetic acid

[*] The carbonium ion-sensitised photochemical reaction of tetracyclone is currently under more detailed examination.

[10] C. F. Wilcox and M. P. Stevens, *J. Amer. Chem. Soc.*, 1962, **84**, 1258; C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *ibid.*, 1968, **90**, 975.

solution was freshly saturated with hexamethylbenzene (conc. *ca.* 10^{-2}M). On allowing the sample to warm to the m.p. of trifluoroacetic acid (-15 °C) while continuing irradiation, the broad signal decreased in intensity and was then replaced quite suddenly by a transient spectrum (Figure 2,B) also centred at $g = 2$ and consisting of at least 11 equally spaced lines with a splitting of *ca.* 6·4 G. This splitting and the number of lines are very similar to those reported for hexamethylbenzene radical cation,[14] although the line-

[11] R. W. Kiser, ' Introduction to Mass Spectrometry and Its Applications,' Prentice-Hall, Englewood Cliffs, 1965, Appendix 4B.

[12] P. S. Engel and B. M. Monroe, *Adv. Photochem.*, 1971, **8**, 245.

[13] D. Olness and H. Sponer, *J. Chem. Phys.*, 1963, **38**, 1782.

[14] R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1965, 1120; R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, 1970, **92**, 412.

width is larger, presumably because of the physical state of the sample. In some experiments, additional less intense lines were discernible between the major lines: these too had an even spacing, ca. 6·1 G. Repetition of the experiment with a solution containing no triphenylmethyl cation gave no e.s.r. signal * Figure 2,C shows the transient spectrum observed when an irradiated solution of triphenylmethyl cation and hexamethylbenzene which had been
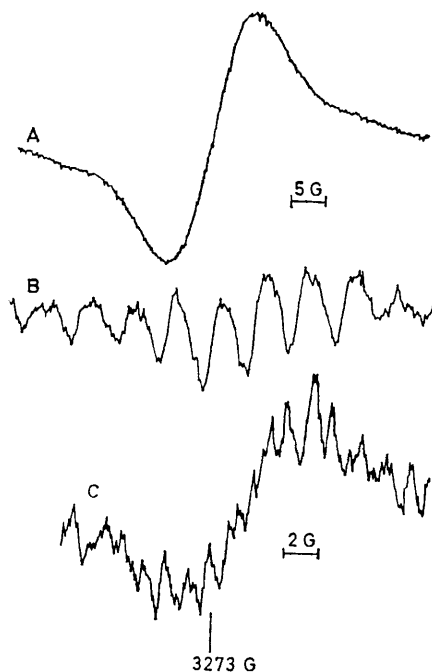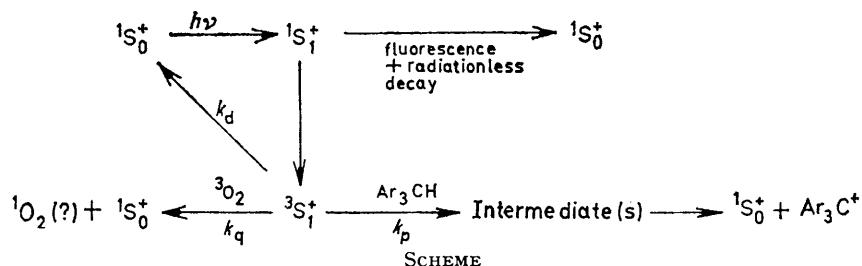

FIGURE 2 E.s.r. spectra of irradiated frozen solutions of triphenylmethyl cation (10^{-3}M) and hexamethylbenzene (ca. 10^{-2}M) in trifluoroacetic acid: A, at -196 °C; B, on warming to ca. -20 °C; receiver gain $50 \times$ A; C, as for B but with rigorous exclusion of oxygen, receiver gain $80 \times$ A (for all spectra, the microwave frequency was $9·225$ GHz and the scan time 4—8 min)

rigorously freed from oxygen by several freeze–pump–thaw cycles was allowed to warm. Many more lines are present,

phenylmethyl radical when triphenylmethyl cation is irradiated in the presence of hexamethylbenzene in trifluoroacetic acid.

DISCUSSION

The photochemical behaviour of the three sensitiser carbonium ions studied in the presence of triarylmethanes in trifluoroacetic acid can be understood with the aid of the Scheme. Initial excitation of the sensitiser cation gives rise to the first excited singlet state ($^1S_1{}^+$). Xanthydryl and 5H-dibenzo[a,d]cycloheptenyl cations show marked fluorescence: much weaker fluorescence is observed for triphenylmethyl cation ($\Phi_f = 0·001$) [2a] as might be expected for this less rigid structure where radiationless decay processes are likely to be more important. Intersystem crossing to the triplet state of the sensitiser cation ($^3S_1{}^+$) competes with fluorescence and radiationless decay of $^1S_1{}^+$. It is this excited triplet carbonium ion which we believe to be responsible for the photo-oxidation. That this is so follows from the failure of triarylmethanes to quench the fluorescence of the sensitisers and our observation of inhibition of photo-oxidation by excess of molecular oxygen. Moreover, excited triplet carbonium ions, including triphenyl-methyl cation, have been detected by e.s.r. spectroscopy in irradiated solid solutions.[16]

From the Scheme, by use of a conventional steady-state treatment, it can readily be shown that the quantum yield for product carbonium ion formation using sensitiser S$^+$ (Φ_S) in the absence of significant oxygen inhibition is given by equation (1) where the superscript

$$^N\Phi_s = \Phi_0 \frac{k_p[\text{Ar}_3\text{CH}]}{k_p[\text{Ar}_3\text{CH}] + k_d} \qquad (1)$$

N signifies the absence of excess of molecular oxygen and Φ_0 is the quantum yield for the formation of $^3S_1{}^+$. Thus we obtain equation (2). In an analogous fashion it can

$$^N\Phi_s{}^{-1} = \Phi_0{}^{-1} (1 + k_d/k_p[\text{Ar}_3\text{CH}]) \qquad (2)$$

be shown that, under conditions where oxygen inhibition

SCHEME

and the separation is now only 1—2 G, the range of values reported for triphenylmethyl radical.[15] In all experiments, e.s.r. signals disappeared when the samples liquefied.

More detailed investigation of this system is in hand, but we tentatively interpret our observations as indicating formation of hexamethylbenzene radical cation and tri-

* Much longer irradiation (>1 h) of freshly prepared frozen solutions of hexamethylbenzene in trifluoroacetic acid, followed by warming, gave a very weak signal at ca. $g = 2$.

occurs, the quantum yield for carbonium ion formation ($^O\Phi_s$) is given by

$$^O\Phi_s{}^{-1} = \Phi_0{}^{-1} \{1 + (k_d + k_q[\text{O}_2])/k_p[\text{Ar}_3\text{CH}]\} \qquad (3)$$

$$= {}^N\Phi_s{}^{-1} \{1 + k_q[\text{O}_2]/(k_d + k_p[\text{Ar}_3\text{CH}])\} \qquad (4)$$

[15] A. L. Buchachenko, ' Stable Radicals,' Consultants Bureau, New York, 1965, ch. 2.
[16] Cf. M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, Mol. Phys., 1966, 10, 241.

That $^{N}\Phi_{s}$ is effectively independent of [Ar$_3$CH] indicates that $k_d \ll k_p$[Ar$_3$CH] in the systems studied. Moreover, values of k_q/k_d in the range 10^6—10^5 l mol^{-1} have been reported[17] for xanthene dyes such as Rose Bengal which are structurally related to xanthydryl cation: while oxygen quenching of triplet states is thought to be diffusion-controlled, k_d should be much smaller since it involves a formally disallowed multiplicity change. Thus equation (2) becomes $^{N}\Phi_{s} = \Phi_{0}$ and equation (3) becomes (5). The dependence of

$$^{O}\Phi_{s}^{-1} = \Phi_{0}^{-1} (1 + k_q[O_2]/k_p[Ar_3CH]) \qquad (5)$$

$^{O}\Phi_{s}$ on [Ar$_3$CH] is thus explained, together with the observed dependence of the slopes of plots of $^{O}\Phi_{s}^{-1}$ against [Ar$_3$CH]$^{-1}$ on the concentration of oxygen in the system. While values of Φ_{0} can in principle be obtained from the intercepts of these same plots at [Ar$_3$CH]$^{-1} = 0$, in practice the intercepts are so small that they cannot be obtained with a satisfactory degree of accuracy from the available data. Instead values of $^{N}\Phi_{s}$ over a range of triarylmethane concentrations have been averaged for each sensitiser. Values so obtained are for xanthydryl cation, 0·095; for triphenylmethyl cation 0·009; for 5H-dibenzo[a,d]cycloheptenyl cation, 0·079.

sensitised by triphenylmethyl cation, k_p must have a value close to the diffusion-controlled limit.

In photo-oxidations sensitised by xanthydryl and 5H-dibenzo[a,d]cycloheptenyl cations, 4-substituents in the triphenylmethane cause marked variations in the observed value of $k_p/k_q[O_2]$. The results for the two series of experiments show roughly parallel changes, attributable to changes in the value of k_p from approximately that for diffusion control to one some two orders of magnitude lower. The effects of the substituents fall in a sequence close to that of decreasing electron repulsion.

Table 8 also includes data which show the influence of 4-substituents on molecular properties which may be relevant to the mechanism of the carbonium ion-sensitised photo-oxidation of triarylmethanes. These properties are (i) the stability of the product carbonium ion as measured by the published values of pK_{R+},[1] (ii) the stability of the corresponding triarylmethyl radical as measured by pK_d, where K_d is the dissociation constant of the triarylmethyl radical dimer in benzene solution,[15] and (iii) the stability of the triarylmethane radical cation for which the ionisation potential of the corresponding substituted benzene[11] has been used in the absence of

TABLE 8

Values of $k_p/k_q[O_2]$ in photo-oxidations of 4-substituted triphenylmethanes and the stabilities of the related carbonium ions, radicals, and radical cations

4-Substituent	$\dfrac{10^{-3}(k_p/k_q[O_2])}{1\ \text{mol}^{-1}}$			pK_R-	pK_D	I.P./eV
	(1)	(2)	(3)			
Ph	3·13	8·44	0·82		−2·4	8·27
MeO	2·31 ^{a}	4·88	0·87	−3·40	−3·1	8·22
Bu^t	2·28	10·3	0·089	−6·1	−2·6	8·68
Me	1·83	6·95	0·055	−5·41	−3·0	8·82
Cl	0·211	10·8	0·105	ca. −7·0 ^{b}	−3·0	9·07
H	0·137	13·1	0·024	−6·63	−3·7	9·24
NO$_2$	0·090	7·3	0·019	−9·15	ca. −1·9 ^{b}	9·92

^{a} 4,4'-Dimethoxytriphenylmethane, 2·74 × 10^3 (pK_{R+}, −1·24); 4,4',4''-Trimethoxytriphenylmethane, 2·85 × 10^3 (pK_{R+}, +0·82). ^{b} By calculation from data for the symmetrically trisubstituted analogue, assuming additivity of substituent effects.

With these values of Φ_{0} and the observed values of $^{O}\Phi_{s}$ at a fixed value of [Ar$_3$CH] and [O$_2$] (Table 6), values of $k_p/k_q[O_2]$ for the series of 4-substituted triphenylmethanes in air-saturated trifluoroacetic acid can be calculated for each sensitiser carbonium ion. The numbers are in Table 8. If it can be assumed that k_q is approximately the same for the three sensitisers (as would be the case if oxygen quenching in these systems is also diffusion-controlled), then the sets of $k_p/k_q[O_2]$ values can be compared directly with each other.

Table 8 shows that the values of $k_p/k_q[O_2]$ for each of the substituted triphenylmethanes are largest for oxidation sensitised by triphenylmethyl cation. With this sensitiser there is a relatively small (less than three-fold) variation in the partitioning ratio with changing 4-substituent, and this does not evince any discernible electronic influence. This is not too surprising since the magnitude of $k_p/k_q[O_2]$ coupled with known values of k_q for other triplet sensitisers and an oxygen concentration of 10^{-3}—10^{-2}M indicates that, in photo-oxidations

measured values for triarylmethanes. These data show rough correlations between all of them and the values of $k_p/k_q[O_2]$ for photo-oxidations sensitised by xanthydryl and dibenzocycloheptenyl cations. The correlation with ionisation potentials of monosubstituted benzenes seems marginally the best and this is shown as a free-energy plot in Figure 3.

Since a value of $k_p/k_q[O_2]$ of the order of 10^3 signifies a value of k_p approaching the diffusion-control limit, the slope of any free-energy correlation should approach zero as log $(k_p/k_q[O_2])$ approaches 3. This is apparent in the results for photo-oxidation sensitised by triphenylmethyl cation (Figure 3, line 2). No mechanistic deduction can be made from such behaviour (but see below). As k_p falls below the value appropriate to a diffusion process, i.e., log $(k_p/k_q[O_2]) < 3$, the results from photo-oxidations sensitised by xanthydryl and dibenzocycloheptenyl cations show a clear correlation with the ionisation potential. Significantly the results for photo-

[17] K. Gollnick, Adv. Photochem., 1968, 6, 1.

oxidation of 4-nitrotriphenylmethane indicate that this compound is oxidised much more readily than would be expected on the basis of a *linear* free-energy correlation with ionisation potentials of monosubstituted benzenes. Now it must be borne in mind that the effect of the nitro-group on the ionisation potential of triphenylmethane is likely to be much less than on the ionisation potential of benzene since 4-nitrotriphenylmethane possesses two phenyl groups similar to the three in triphenylmethane itself from which an electron may be excited. Consistent with this is the observation that $k_p/k_q[O_2]$ for 4-nitrotriphenylmethane is roughly two-thirds of its value for triphenylmethane with all three sensitiser cations. Such an observation is not consistent with either hydride-ion or hydrogen-atom abstraction by the excited sensitiser
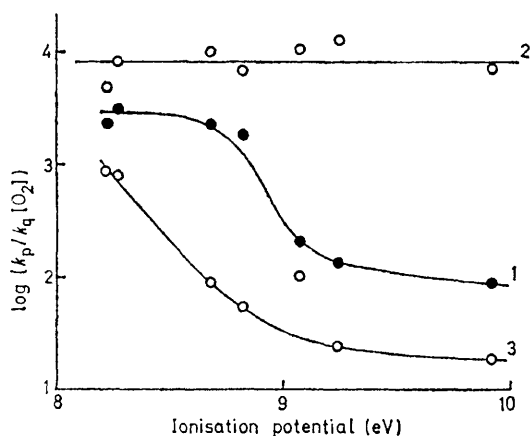

FIGURE 3 Effect of 4-substituents on the reactivity of triphenylmethane in photo-oxidations sensitised by carbonium ions (1), (2), and (3)

from the α-carbon atom since these would involve a direct interaction of the substituent and the reaction site leading to a large effect of the nitro-substituent on k_p. This argument suggests that correlations between log $(k_p/k_q[O_2])$ and pK_{R^+} or pK_d are inappropriate.
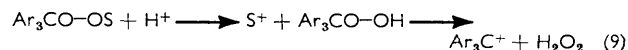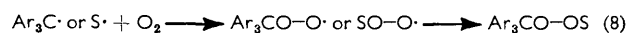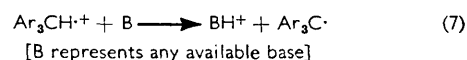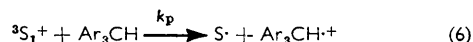
The observations from experiments with hexamethylbenzene confirm the correctness of the correlation with ionisation potential. The e.s.r. spectroscopic evidence indicates that irradiation of triphenylmethyl cation in the presence of hexamethylbenzene leads to the formation of hexamethylbenzene radical cation, by electron transfer from the hydrocarbon to the carbonium ion. Moreover, the ionisation potential of hexamethylbenzene (7·82 eV) is considerably lower than that of triphenylmethane (8·55 eV),* so that it should be able to compete effectively with triphenylmethane in electron transfer to a triplet sensitiser carbonium ion and hence quench the photo-oxidation. Quenching by hexamethylbenz-

* We are indebted to Mr. F. A. Mellon of these laboratories for the determination of this value by photo-electron spectroscopy. A value of 8·80 eV by electron impact has been reported.[18]

† Fluorenone, a less efficient quencher than hexamethylbenzene of xanthydryl cation-sensitised photo-oxidation, has $E_T = 53·3$ kcal mol⁻¹. For comparison, triphenylmethane has $E_T = 81·3$ kcal mol⁻¹.

ene cannot be ascribed to hydride transfer: the carbonium ion which would result from such a process, pentamethylbenzyl cation, can be estimated to have a pK_{R^+} value of *ca.* −16 from the values for 2,4,6-trimethylbenzyl cation (−17·2) and αα,2,3,4,5,6-heptamethylbenzyl cation (−12·4),[19] indicating a much lower stability than any of the triarylmethyl cations whose formation has been investigated. Nor can triplet energy transfer from the sensitiser to hexamethylbenzene explain the quenching: E_T for hexamethylbenzene is probably *ca.* 78 kcal mol⁻¹ (*cf.* toluene 82·3, durene 79·8 kcal mol⁻¹)[12] compared with a reported [2a,b] E_T for triphenylmethyl cation of 50 kcal mol⁻¹.†

The rapidity of the reaction between the triplet carbonium ions and triarylmethanes, the correlation of $k_p/k_q[O_2]$ with ionisation potentials of monosubstituted benzenes, and the quenching results all point to electron transfer from triarylmethane to excited sensitiser as the first step in the photo-oxidation. The immediate products of such a process would be the triarylmethane radical-cation and the radical derived from the sensitiser [equation (6)]. Our experiments do not provide direct evidence concerning the subsequent steps in the photo-oxidation, but those shown in equations (7)—(9) seem plausible though not unique.[1,20]

$$^3S_1^+ + Ar_3CH \xrightarrow{k_p} S\cdot + Ar_3CH\cdot^+ \qquad (6)$$

$$Ar_3CH\cdot^+ + B \longrightarrow BH^+ + Ar_3C\cdot \qquad (7)$$
[B represents any available base]

$$Ar_3C\cdot \text{ or } S\cdot + O_2 \longrightarrow Ar_3CO-O\cdot \text{ or } SO-O\cdot \longrightarrow Ar_3CO-OS \quad (8)$$

$$Ar_3CO-OS + H^+ \longrightarrow S^+ + Ar_3CO-OH \longrightarrow Ar_3C^+ + H_2O_2 \quad (9)$$

This interpretation accounts satisfactorily for our failure to observe significant deuterium isotope effects on quantum yields for photo-oxidation of α-deuteriotriphenylmethane and its 4-methoxy-analogue. In oxidations sensitised by triphenylmethyl cation, this is because the rate of reaction of the hydrocarbon and excited sensitiser is diffusion-controlled. In xanthydryl cation-sensitised photo-oxidation, at least of triphenylmethane, the product-forming step does not occur on every collision between the excited sensitiser and hydrocarbon: the absence of a deuterium isotope effect here is therefore evidence for a mechanism not involving cleavage of the α-carbon–hydrogen bond.[21]

Electron abstraction by photochemically-excited carbonium ions has previously been suggested as the first step in the conversion of triphenylcyclopropenyl cation into hexaphenylbenzene; dimerisation of the intermediate triphenylcyclopropenyl radical with subsequent rearrangements is thought to complete the reaction.

[18] V. K. Potapov, D. N. Shigorin, A. D. Filyugina, and V. V. Sorokin, *Russ. J. Phys. Chem.*, 1966, **40**, 1256.

[19] N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Amer. Chem. Soc.*, 1960, **82**, 4719.

[20] D. E. Bissing, C. A. Matuszak, and W. E. McEwen, *J. Amer. Chem. Soc.*, 1964, **86**, 3824.

[21] *Cf.* G. W. Cowell, A. Ledwith, A. C. White, and H. J. Woods, *J. Chem. Soc. (B)*, 1970, 227; G. R. Chalfont and M. J. Perkins *ibid.*, 1971, 245.

Hydrogen-atom abstraction has, however, been suggested as the preferred mode of reaction for excited triplet triphenylmethyl cations in aqueous sulphuric acid or sulphuric–acetic acid mixtures [2c] (but see ref. [2b]). Under air-free conditions in the latter solvent, triphenylmethane, 9-phenylfluorene, and, surprisingly, the corresponding peroxide were formed. Addition of cumene, toluene, or cyclohexane (*ca.* 10^{-2}M) caused accelerations in the rate of removal of triphenylmethyl cation in the ratio $11.2 : 1 : 0.37$, and this ' selectivity ' was interpreted as supporting hydrogen abstraction as the primary reaction of the excited carbonium ions, the resultant radical cation, after loss of a proton, combining with the synchronously formed radical [equation (10)]. Such radical combination products were indeed observed. However, the ' selectivity ' sequence is not only the sequence of increasing C–H bond dissociation energy but

$$^3Ph_3C^+ + RH \longrightarrow R\cdot + Ph_3CH\cdot^+ \longrightarrow Ph_3C\cdot \longrightarrow Ph_3CR \quad (10)$$
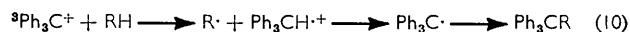
also that of increasing ionisation potential. The ' selectivities ' are thus equally consistent with initial electron transfer from RH to the triplet carbonium ion, giving the radical cation $RH\cdot^+$ and triphenylmethyl radical. The ultimate chemical consequence of initial electron transfer would then be the same as on a hydrogen atom transfer mechanism.

EXPERIMENTAL

All photochemical experiments were conducted at room temperature.

Materials.—Trifluoroacetic acid, b.p. 72 °C, was fractionated through a 1-m helix-packed column immediately before use.

Substituted triphenylmethanes were prepared by literature methods. Most were obtained by reduction of the corresponding triphenylmethanol with isopropyl alcohol in concentrated sulphuric acid.[22] Methoxytriphenylmethanes were prepared by refluxing anisole with the corresponding diarylmethanol in benzene containing toluene-*p*-sulphonic acid, water being removed continuously.[23] 4-Nitrotriphenylmethane was prepared by the method of Curtin and Kauer.[24] Physical properties agreed closely with those in the literature. *4-t-Butyltriphenylmethane*, m.p. 67—69 °C, has not been described hitherto (Found: C, 92.0; H, 8.05. $C_{23}H_{24}$ requires C, 91.95; H, 8.05%).

α-Deuteriotriphenylmethane was prepared by decomposition of triphenylmethylmagnesium bromide with deuterium oxide. Reaction of α-deuteriodiphenylmethanol with anisole as indicated above yielded α-deuterio-4-methoxytriphenylmethane. Both these hydrocarbons were more than 95% α-deuteriated as indicated by ^1H n.m.r. spectroscopy.

Substituted triphenylmethanols were prepared by reaction of phenylmagnesium bromide with the ethyl ester of the appropriate *para*-substituted benzoic acid. M.p.s were in agreement with literature values except for 4-phenyltri-

* Ref. 25 gives the m.p. of 3-phenyltriphenylmethanol as 104.8—105.6 °C. The origin of our material, the ^1H n.m.r. spectrum of the intermediate ester, and the close agreement of the visible spectrum of the derived carbonium ion with that in the literature for the 4-phenyltriphenylmethyl cation convince us of the authenticity of our 4-phenyltriphenylmethanol.

phenylmethanol. This compound had m.p. 105—106 °C (lit.,[25] 136.4—137.2 °C) (Found: C, 89.4; H, 6.2. Calc. for $C_{25}H_{20}O$: C, 89.25; H, 6.0).* There is no previous report of *4-t-butyltriphenylmethanol*, m.p. 41—42 °C (Found: C, 87.2; H, 7.8. $C_{23}H_{24}O$ requires C, 87.3; H, 7.65%).

Visible spectral data for the product carbonium ions, derived from the triarylmethanols by dissolution in trifluoroacetic acid containing 1% (v/v) acetic acid, are in Table 9.

TABLE 9

Visible maxima in the electronic spectrum of 4-substituted triphenylmethyl cations in trifluoroacetic acid containing 1% (v/v) acetic acid

4-Substnt.	$\lambda_{max.}$/nm	$\varepsilon_{max.}$
H	410	40,000
	425	39,000
Ph	411	20,000
	515	53,700
MeO [a]	390	16,000
	468	60,000
Bu^t	450	55,300
Me	446	54,200
Cl	444	36,800
NO$_2$	385	33,500
	443	36,800

[a] 4,4'-Dimethoxytriphenylmethyl cation: $\lambda_{max.}$ 408 nm (38,200), 494 nm (85,200); 4,4',4''-Trimethoxytriphenylmethyl cation: $\lambda_{max.}$ 478 nm (115,000).

Quantum Yield Determinations.—Quantum yields for carbonium ion formation from triarylmethanes were determined by conventional means.[9] The light source was a 250 W Mazda type ME/D medium-pressure mercury arc. A band in the output of the source appropriate to a long-wavelength absorption peak of the sensitiser cation was selected by means of an interference filter (Schott and Gen.; band-width at half the maximum intensity of transmitted light, ≤10 nm). The filtered light was passed through a cylindrical glass cell (diam. 50 mm; optical path 10 mm) containing a solution of the triarylmethane and sensitiser prepared by dilution of concentrated stock solutions of the reactants in acetic acid (or, in some cases, methanol) with freshly distilled trifluoroacetic acid. The proportion of solvent other than trifluoroacetic acid never exceeded 4% and never reduced the acidity of the medium below the level at which the carbonium ions are formed virtually completely from the corresponding triarylmethanol. The reaction solution was continuously flushed (20—25 ml min⁻¹) with oxygen or a mixture of oxygen and nitrogen which had been dried by passage over calcium chloride and pre-saturated with solvent. Quantum yields were independent of the rate of flow of gas. Samples of the solution were withdrawn at intervals and the concentration of carbonium ion determined spectrophotometrically. Quantum yields were then evaluated from the slope of linear plots of optical density of the samples, measured at the wavelength of maximum absorption of the carbonium ion, against time. The extent of conversion of triarylmethane was always less than 8%. The intensity of the light emitted by the source and passed by the filter was monitored at frequent intervals during the course of the investigation;

[22] P. D. Bartlett and J. D. McCollum, *J. Amer. Chem. Soc.*, 1956, **78**, 1441.

[23] E. F. Pratt and L. Q. Green, *J. Amer. Chem. Soc.*, 1953, **75**, 275.

[24] D. Y. Curtin and J. Kauer, *J. Org. Chem.*, 1960, **25**, 880.

[25] N. N. Lichtin and H. Glazer, *J. Amer. Chem. Soc.*, 1951, **73**, 5537.

ferrioxalate actinometry was used. Quantum yields so determined were reproducible within $\pm 3\%$ with use of different light sources as well as different solutions.

Instrumentation.—Fluorescence spectra were recorded on a Perkin-Elmer type 204 spectrofluorimeter. A Varian E4 instrument was used for the e.s.r. experiments.