

REVIEW PAPER:

INTERMOLECULAR PHOTOREDUCTIONS OF KETONES

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INTRODUCTION AND SCOPE

The photoreduction of carbonyl compounds can be represented by:



where $>\text{CO}^*$ represents an electronically excited carbonyl group, frequently a thermally equilibrated lowest triplet state. X and Y can be atoms or group of atoms. Three out of the four possible combinations have been detected, and some examples are shown in Table 1.

Some aspects of the subject have been considered in previous reviews. For example, Howard⁶, in a recent review dealt with some aspects of radical-like hydrogen abstraction. Turro *et al.*⁷ reviewed the photochemistry of alkanones in solution, intermolecular hydrogen abstraction being among the reactions examined.

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TABLE 1
EXAMPLES OF PHOTOREDUCTION OF CARBONYL COMPOUNDS

X-Y	<i>e.g.</i> X	<i>e.g.</i> Y	>CO	Reference
1. atom-atom	H	Br	Acetone	1
2. atom-group	H	PhCH ₂	Acetophenone	2
	H	SiH ₃	Acetone	3
3. group-group	BBu ₂	Bu	Acetone	4
	Sn(Cl)Pr ₂	Pr	Acetophenone	5
4. group-atom	—	—	—	not reported

Some aspects of photoreduction involving attack at multivalent centres have been reviewed by Davies and Roberts⁸.

The subject has also been dealt with in the various annual surveys of the literature⁹.

Porter¹⁰ has discussed the importance of the electron distribution in the excited state in determining its reactivity.

This review is not intended to be exhaustive. Its purpose is to bring together different aspects of the same problem, which, for practical reasons or reflecting the interests of the reviewers, have usually been dealt with as sections in reviews covering other aspects of photochemistry or of free radical chemistry.

The aspects of reaction (1) to be examined are those directly related to its mechanism, kinetics and quantum yield. The processes by which >CO* molecules are produced, or by which the radicals >COX and Y· are removed will not be examined in detail unless they are directly relevant to the understanding of the elementary step represented by reaction (1). Most of the emphasis is placed on monoketones.

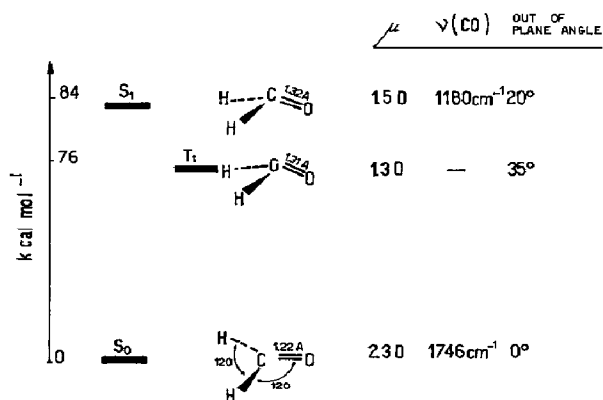
Although as pointed out above, this review is not exhaustive, an attempt has been made to include all those references which contain original interpretations or in which a considerable amount of quantitative data is reported. Some late 1972 relevant references might have been omitted.

THE NATURE OF THE EXCITED STATES

The first excited singlet and triplet states of the simplest carbonyl compound, formaldehyde, are well characterized. An examination of their characteristics is useful in the understanding of the electronic properties of alkanones. The scheme on page 83 summarizes the most relevant properties^{7, 11-16}.

Both states (S₁ and T₁) are *n*, π* in character. The *n* orbital is mainly localized in the carbonyl oxygen atom, while the π* orbital is delocalized over the carbonyl function^{7, 11}. The excited states are electrophilic and radical-like in the proximity of the oxygen atom and nucleophilic above and below the carbonyl faces (due to the π* electron)^{7, 11}.

Excited aliphatic ketones are likely to be nearly planar¹¹. For acetone the energy of the lowest triplet is about 79-80 kcal mol⁻¹.



In the case of aromatic carbonyl compounds the excited state associated with the aromatic ring is frequently mixed into the lowest excited states; the reactivity of the excited molecule will depend on the contribution of this π, π^* state. For many aromatic ketones (*e.g.* acetophenone) the two triplet states, having mainly n, π^* and π, π^* character, are very close and substituent or solvent effects can lead to an inversion of states. For example the lowest triplet state of acetophenone is n, π^* in character, ($E_t = 74 \text{ kcal mol}^{-1}$), while for *p*-methoxy-acetophenone it is π, π^* in character ($E_t = 72 \text{ kcal mol}^{-1}$)^{11, 17}.

Lamola¹⁸ has examined in detail the characteristics of the excited states of acetophenone. He concluded that in hydrocarbon glass the low lying triplet is n, π^* in character. In polar solvents the short-lived phosphorescence from the former is replaced by a longer-lived phosphorescence, characteristic of the π, π^* state (³La). He also pointed out that intersystem crossing in acetophenone is likely to proceed from the ¹ n, π^* state to the ³La state. This is consistent with the fact that spin-orbit coupling between ¹ n, π^* and ³ π, π^* states is allowed¹⁹.

Medium effects on the characteristics of the excited states have also been examined by Leermakers *et al.*²⁰ and by Lindqvist *et al.*²¹ and Lutz²² and Wagner *et al.*²³. n, π^* transitions show a blue shift in the presence of hydroxylic solvents due to the hydrogen bonding. This shift is partly responsible for the inversion of states mentioned above¹⁰.

The ³ n, π^* state is frequently considered as a biradical, formally having seven electrons around a single bonded oxygen atom^{10, 14, 24, 25}. In agreement with this assumption, alkoxy radicals have been found to be good analogues of n, π^* carbonyl triplets in relation to their behaviour in radical-like reactions²⁶⁻²⁹. These ideas are further developed in a later section.

EXPERIMENTAL RESULTS ON HYDROGEN ABSTRACTIONS

Photoreduction reactions involving hydrogen abstractions are usually divided into radical-like and charge transfer processes. This classification is also used in

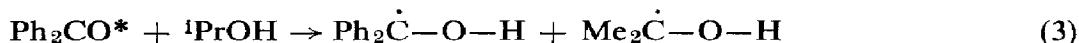
this review; however, we note that they are probably limiting cases of a single mechanism which involves both interactions simultaneously. Moreover, the relative importance of these two types of interaction might be largely dependent upon the characteristics of the medium.

Radical-like abstractions

This section deals with reactions which involve hydrogen atom transfer, reaction (2), and in which, to the best of our knowledge charge-transfer interactions are not important, *i.e.* we will be concerned with those processes which can be rationalized on the basis of a mechanism involving the *simultaneous* one step cleavage of the R-H bond and formation of the O-H bond to yield two electrically neutral species. This is in fact the most common type of photoreduction and has been extensively studied.



The most studied system is probably the photoreduction of benzophenone triplets by isopropanol:



for which the rate constant at room temperature is $\sim 1.3 \times 10^6 M^{-1} s^{-1}$ ³⁰.

Padwa²⁶, and independently Walling and Gibian²⁷ suggested that alkoxy radicals are excellent analogues of carbonyl triplets in hydrogen abstraction processes and the idea is widely accepted nowadays (see also refs. 10 and 14).

Electron spin resonance (e.s.r.) studies have provided clear-cut evidence of the production of ketyl radicals³¹⁻³⁶ as intermediates in the reaction and several of the studies have also been concerned with the rate of self-termination of the radicals produced by irradiation of ketone-hydrogen donor systems³⁷⁻⁴⁰.

Flash techniques have allowed the study of the effect of different substrates on the lifetime of the excited ketone, as well as verify the formation of radicals in the quenching by hydrogen donors^{21, 22, 41-46}. Most of these studies were made possible by the recent development of the nanosecond flash photolysis by Porter and Topp⁴¹.

Flash or e.s.r. techniques (and eventually the combination of both)⁴⁷ are excellent methods for the study of these reactions; however, most of the data currently available have been obtained by conventional quenching and analytical techniques. These usually involve the measurement of the quantum yield of ketone disappearance, product formation, or occurrence of a competitive process, under conditions in which the photoreduction reaction competes with other processes, the rate of which is known or can be estimated. The competitive processes can be classified in two groups: (i) a bimolecular process which removes the reactive excited species from the medium, *i.e.* bimolecular quenching. In general physical quenchers are preferred against chemical quenchers: (ii) a unimolecular process

which can compete with the intermolecular photoreduction. The technique has not been frequently employed in solution. The processes which can be considered in this group are emission (fluorescence or phosphorescence)²⁵ and Types I and II photoeliminations.

Quite frequently the reaction proceeds exclusively from the triplet state. This conclusion is supported by the fact that in general selective "triplet" quenchers such as 1,3-dienes are quantitative quenchers of the reaction and that hydrogen donors do not usually quench fluorescence. Carbonyl triplet quenching by conjugated dienes proceeds *via* energy transfer. Some chemical quenching (leading to oxethanes) also takes place, but this can be regarded as an inefficient process. For example, for the benzophenone/2,3-dimethyl-1,3-butadiene system in benzene the rate constant for photocycloaddition is $\sim 1.5 \times 10^6 M^{-1} s^{-1}$ ⁴⁸.

Several recent reports⁴⁹⁻⁵³ indicate that dienes also quench the singlet state of carbonyl compounds. Yang *et al.*⁵⁰ have shown that fluorescence quenching and oxethane formation by dienes proceed *via* the same intermediate. Penta-1,3-diene has been found to be less efficient than cyclohexa-1,3-diene^{49, 50}. For example, in the case of acetone singlets the values of $k_q\tau$ for *cis*-penta-1,3-diene and cyclohexa-1,3-diene are 0.19 and 1.45 M^{-1} respectively⁵⁰. For penta-1,3-diene concentrations below 0.1 M the interaction with the singlet state can be frequently neglected.

The detection of a singlet contribution in the photoreduction of acetone has been attempted by Wagner⁵⁴ using tri-*n*-butyl stannate as hydrogen donor. The reaction was found to occur exclusively from the triplet state, the lack of reactivity of the singlet state being due to "true" unreactivity, rather than to a short lifetime of the singlet; however, Turro *et al.*^{7, 55} have noted that several secondary reactions can vitiate standard kinetic analysis in this system. It has also been reported that the fluorescence from 2-adamantanone is quenched by tri-*n*-butyl stannate with a rate constant of $5 \times 10^8 M^{-1} s^{-1}$ ⁵⁶. In the gas phase Yarwood⁵⁷ has recently examined the quenching of the fluorescence from chloropentafluoroacetone by several hydrocarbons at 23°C and at pressures where the reaction can be attributed to thermalized singlets. He found that the rates of quenching are dependent upon the nature of the more reactive C-H bonds (tertiary > secondary > primary). Although the products were not examined the process might conceivably involve hydrogen abstraction*. His results are summarized in Table 2. Germane was also found to be very efficient.

The singlet reaction is far from being understood and we can only hope that future examination will throw more light on this aspect of the reaction. Turro¹¹ has pointed out that the apparent lack of reactivity of the singlet state of aromatic ketones is certainly a reflection of the short lifetime of S_1 rather than a lack of

* An alternative explanation might be that the changes in rate constant reflect changes in cross-section. With the exceptions of *n*-pentane and 2,2-dimethyl propane the values can be reasonably correlated on this basis too.

inherent reactivity of S_1 . Porter¹⁰ has pointed out that one might expect the reactivities of singlet and triplet to differ very little in the case of n,π^* states, the lack of reactivity of the singlet state being due to a rapid intersystem crossing, but not necessarily implying a different rate constant. Hereafter, unless otherwise indicated we will refer to reactions of the triplet state.

Several studies have been concerned with the measurement of the quantum yield of photoreduction for many ketone-substrate pairs and several concentrations and media. Table 3 shows a summary of quantum yields for several ketones in isopropanol.

TABLE 2

FLUORESCENCE QUENCHING DATA FOR CHLOROPENTAFLUOROACETONE IN THE GAS PHASE AT 23°C ($\lambda = 313$ NM; $P = 200$ TORR)

Quencher	$k(\text{exp.})^{\text{a, b, c}}$	$k(\text{calc.})^{\text{b, d}}$
Ethane	5.0×10^7	5.0×10^7
Propane	4.1×10^8	4.1×10^8
n-Butane	9.4×10^8	7.7×10^8
2-Methylpropane	1.0×10^9	1.0×10^9
n-Pentane	9.0×10^8	11.3×10^8
2-Methyl butane	1.5×10^9	1.4×10^9
2,2-Dimethyl propane	3.0×10^8	1.0×10^8
Cyclopentane	3.7×10^9	1.8×10^9
2,3-Dimethyl butane	2.5×10^9	1.9×10^9
Germane	2.5×10^9	—

^a Taken from ref. 57.

^b in units of $M^{-1} s^{-1}$.

^c Using τ (chloropentafluoroacetone singlets) = 3.5×10^{-8} s.

^d Calculated assuming that the reactivity of $-\text{CH}_3$ groups is $1/2k$ (ethane), the reactivity of $>\text{CH}_2$ groups k (propane) $-k$ (ethane) and the reactivity of $\geq\text{CH}$ groups $k(2\text{-methyl propane}) - 3/2 k$ (ethane), and adding group contributions for each substrate.

TABLE 3

QUANTUM YIELDS FOR THE PHOTOREDUCTION OF AROMATIC KETONES BY ISOPROPANOL

Ketone	$[\text{PrOH}]/M$	Solvent	$\tau_{\text{rad/sec}}$	Φ_{-K}	Ref.
acetophenone (ACP)	neat	—	0.005 ^a	0.68	58
<i>p</i> -methyl-ACP	neat	—	0.14	0.66	58
<i>m</i> -methyl-ACP	neat	—	0.12	0.46	58
3,4-dimethyl-ACP	neat	—	0.30	0.12	58
<i>p</i> -methoxy-ACP	neat	—	0.38	0.04	58
3,5-dimethyl-ACP	neat	—	0.20	0.018	58
3,4,5-trimethyl-ACP	neat	—	0.42	0.018	58
<i>m</i> -methoxy-ACP	neat	—	0.71	0.006	58
benzophenone	0.05	benzene	—	0.45	59
benzophenone	0.50	benzene	—	1.41	59
camphorquinone	neat	—	—	0.057	60 ^b

^a See also ref. 65.

^b The photoreduction of camphorquinone has been frequently examined; see refs. 61–64.

Yang *et al.*⁵⁸ have found an inverse correlation between the quantum yield of photoreduction and the radiative lifetime of the triplet (see Table 3).

Several reports in the early 1960s^{26, 27, 66-68} were concerned with mechanistic aspects and the measurement of relative rate constants. Some absolute rate constants were also reported; several of these rate constants are not consistent with more recent studies and this can be frequently attributed to erroneous assumptions regarding the rates of quenching or the use of non-specific quenchers. Table 4 gives a series of relative rate constants (relative to toluene) for benzophenone triplets. The work by Padwa²⁶ also includes acetophenone, butyrophenone and 4-methylbenzophenone. The third column in Table 4 shows the relative values for t-butoxy radicals, which are generally considered to be good analogues of n,π^* ketone triplets²⁵⁻²⁹. The data show dependence with the lability of the hydrogen atom being transferred; furthermore, a closer look shows that another relevant factor is the number of equivalent hydrogen atoms available for reaction.

Another important parameter in determining the rate of reaction is the triplet state energy. For a series of typical ketones the following trend is usually observed^{25, 69-72}:



The other important factor is the nature of the excited state. Ketones having low lying π,π^* triplet states are less reactive than those having low lying n,π^* states. Table 5 shows the data obtained by Yang and Dusenbery⁷³ for four ketones. The higher reactivity of *p*-trifluoromethylacetophenone compared with

TABLE 4

RELATIVE RATE CONSTANTS FOR THE REACTION OF BENZOPHENONE TRIPLETS WITH HYDROGEN DONORS IN BENZENE

Substrate	Rate	Rate(^t BuO) 40°C	Ref.
benzhydrol	256	—	68
<i>p</i> -methoxy toluene	10.6	—	27
2-octanol	10.2	—	27
2-propanol	9.7	—	27
mesitylene	5.5	4.01	26, 27
<i>p</i> -xylene	4.3	—	27
cumene	3.4	—	27, 68
	2.9	2.80	26
<i>m</i> -xylene	2.9	—	27
ethylbenzene	3.05	2.30	26
cyclohexane	2.2	—	27
	4.1	6.0	26
2,3-dimethylbutane	2.0	—	27
	0.84	3.15	26
toluene	1.0	1.0	—
anisole	0.53	—	27
<i>t</i> -butylbenzene	0.26	0.32	26

TABLE 5

EFFECT OF THE NATURE OF THE EXCITED STATE ON PHOTOCHEMICAL REACTIVITY. PHOTOREDUCTION OF AROMATIC KETONES IN 2 *M* ISOPROPANOL IN BENZENE^{a,e}

Ketone ^b	n,π^* (nm)	π,π^* (nm) ^c	$k_r \times 2M \times 10^{-4}$
<i>p</i> -Trifluoromethyl-ACP	397 (emission)	(383)	552
ACP ^d	386 (emission)	(373)	86.6
<i>p</i> -Methyl-ACP	368 (absorption)	392	7.88
3,4-Dimethyl-ACP	367 (absorption)	399	1.68

^a From ref. 78.^b Acetophenone.^c From emission data.^d See also ref. 18.^e A similar study was carried out for substituted benzophenones; see ref. 74.

that of acetophenone reflects the larger energy gap between the first and second triplets (the lower having n,π^* character).

The nature of substituent effects observed parallels very well⁷⁵ the one observed in Type II photoelimination and photocyclization reactions. As pointed out earlier the inversion of states can be achieved not only by substitution in the aromatic ring but also by introducing changes in the polarity and hydrogen bonding properties of the solvent. In a recent study Lutz *et al.*²¹ have examined the solvent dependence of the photoreduction of acetophenone in isopropanol-benzene mixtures by nanosecond laser technique. Isopropanol was used as substrate and polar co-solvent. Some of their results are summarized in Table 6, together with analogous results obtained by Lewis⁶⁹ and data from Table 3.

Two types of interpretation have been given to the low reactivity of ketones having a low lying π,π^* triplet⁷⁵: (i) an equilibration of states leads to the presence of both types of triplet, the $^3n,\pi^*$ one being reactive; and (ii) vibronic mixing leads to "mixed character". The former mechanism is likely to be applicable when the energy gap between both triplet states is small, and it can easily be expressed quantitatively. Mechanism (ii) is probably more important for large energy gaps but, of course, both can always be applicable and it is only their relative importance that changes.

The lack of dependence with solvent polarity in the case of benzophenone (see Table 6) can be attributed to the larger energy gap between n,π^* and π,π^* triplets⁷⁷.

Traynard and Blanchi⁷⁸⁻⁸⁰ have examined the photoreduction of a series of heteroaromatic ketones having low lying n,π^* states and found a correlation between "reactivity" and charge on the oxygen atom. Unfortunately most of their studies only involve quantum yields and it is not clear to what extent the same ideas apply to rate constants. A similar study has been carried out by Wagner and Capen for some Type II photoeliminations⁸¹. Suppan⁸² had predicted that this

type of effect could be expected if the reactions have an important electrostatic contribution. Suppan's model is discussed later.

Several recent studies^{41, 44} have examined the lifetime of aromatic ketone triplets in various solvents by flash and other techniques. Some of the values are given in Table 7. In some cases these values can be correlated with the rate of abstraction from the solvent [*i.e.*, when unimolecular triplet decay (radiative or radiationless), physical quenching by the solvent and triplet-triplet annihilation can be neglected]. The lifetime in cyclohexane is shorter for acetophenone than for benzophenone. This can be correlated to a higher reactivity of acetophenone triplets, as expected from the higher triplet energy of acetophenone. However, in isopropanol and ethanol the lifetime is longer for acetophenone, an effect which can be correlated with the inversion of states which takes place in this ketone in polar solvents^{18, 20, 23}. Benzophenone has a larger energy gap and is less sensitive than acetophenone towards solvent effects^{77, 89}.

Hammond *et al.*⁹⁰ have measured the isotope effect in the photoreduction of benzophenone triplets by benzhydrol and benzhydrol-d₁ and found:

$$k_{\text{H}}/k_{\text{D}} = 2.7$$

Similarly Yip and Siebrand⁹¹ report a value of 3.8 for the isotope effect in the photoreduction of acetone triplets by methanol and methanol-d₄.

Turro and Engel⁷¹ have examined deuterium isotope effects in the quenching of biacetyl phosphorescence (in benzene) by various substrates.

Table 8 shows a selection of experimental rate constants for the photoreduction of various ketone triplets in solution for examples where a C-H bond is cleaved.

TABLE 6

EFFECT OF THE COMPOSITION OF ISOPROPANOL-BENZENE MIXTURES ON THE RATE OF PHOTOREDUCTION OF SOME AROMATIC KETONES

Ketone	[¹ PrOH]	$k \times 10^5/M^{-1} \text{ s}^{-1}$	Ref.
Acetophenone	0	18	21
	2.0	12.2	21
	4.0	9.0	21
	8.0	6.5	21
	Neat	6.6	21
	0.1	6.8	76
	0.5	7.5	76
	2.0	7.5	76
	2.0	4.3	73
	<i>p</i> -Methyl acetophenone	0	2.4
2.0		1.7	22
4.0		1.0	22
8.0		0.7	22
Neat		0.95	22
2.0		0.39	73
Benzophenone	O-Neat	10.7	21

TABLE 7

UNIMOLECULAR DECAY RATE CONSTANTS FOR SOME KETONE TRIPLETS IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

Ketone	Solvent	$(1/\tau) \times 10^{-6}/\text{s}^{-1}$	Ref.
Benzophenone	isopropanol	22	41
	ethanol	9.7	41
	dioxane	5.0	41
	cyclohexane	3.3	41
	benzene	0.40	41
		0.20	83
		0.1	84
		0.12	85
	benzene-d ₆	0.29	41
		0.08	84
	benzene-f ₆	2.30	41
		1.40	84
	iso-octane	0.50	83
	water	0.005	43
	perfluoromethylcyclohexane	0.0014	85, 86
carbon tetrachloride	0.009	85	
Acetophenone	isopropanol	9.0	44
	ethanol	7.1	44
	cyclohexane	4.4	44
	toluene	2.2	44
	benzene	0.33	44
		0.30	83
	water	~ 0.01	43
	perfluoromethylcyclohexane	0.0026	86
Acetone	acetone	≥ 0.02	87
	hexane	~ 2.5	88
	perfluoromethylcyclohexane	0.0034	85
<i>p</i> -Methoxybenzophenone	perfluoromethylcyclohexane	0.0017	85
Methyl-2-naphthylketone	perfluoromethylcyclohexane	0.0017	85

A close examination of Table 8 clearly suggests that the triplet energy, the nature of the excited state, the bond dissociation energy and the number of equally reactive hydrogen atoms are the main factors which determine the rates of reaction.

Only a few studies have been concerned with the abstraction of hydrogen atoms bonded to elements other than carbon. Table 9 shows some of the results; most of the studies involve the cleavage of the tin-hydrogen bond in trialkyl stannates, particularly tri-*n*-butyl stannate^{46, 54, 67, 71, 92, 103}. No close examinations seem to have been carried out of the possibility of cleaving the O-H bond in alcohols or hydroperoxides. Turro and Engel⁷¹ have reported that phenols are very efficient quenchers of biacetyl fluorescence and phosphorescence (see also ref. 69). The authors propose that reversible abstraction can account for their results (little or no chemical change occurred).

TABLE 8

RATE CONSTANTS FOR SOME PHOTOREDUCTIONS IN SOLUTION

Ketone	Substrate	Conditions ^a	Compet. to ^{a, b}	log <i>k</i> ^c	Ref.
Acetone	cyclohexane	ACN, RT	—	5.50	42, 91
	<i>t</i> -butanol	ACN, RT	—	3.64	42, 91
	methanol	RT	—	5.00	91
	acetone	RT	—	3.53	91
	acetonitrile	RT	—	3.04	91
Acetophenone ^d	isopropanol ^e	B, 25° C, <i>i</i> PrOH → 0	—	6.26	21
	isopropanol	Neat, 25° C	—	5.82	21
	isopropanol	W, 25° C	—	4.70	21
	cyclohexane ^f	RT	—	5.66	44, 91
	<i>t</i> -butyl benzene	(B ?), RT	TL	4.85	26
	toluene ^f	RT	—	5.37	44, 72
	mesitylene	(B ?), RT	TL	6.11	26
	ethyl benzene	(B ?), RT	TL	5.85	26
	cumene	(B ?), RT	TL	5.79	26
	2,3-dimethylbutane	(B ?), RT	TL	5.30	26
Benzophenone	isopropanol ^g	B, RT	—	6.10	21, 30
	cyclohexane	Neat, RT	—	5.56	41, 72, 91
	ethanol	Neat, RT	—	5.75	41
	tetrabutyltin	B, RT	—	5.85	92
	dioxane ^f	Neat, RT	—	5.63	41, 72
	benzene	B—CCl ₄ , RT	—	1.28	93
	toluene	B, 22° C	CY	5.22	27
	<i>p</i> -methoxytoluene	B, 22° C	CY	6.28	27
	2-octanol	B, 22° C	CY	6.22	27
	mesitylene	B, 22° C	CY	5.97	27
	<i>p</i> -xylene	B, 22° C	CY	5.85	27
	cumene	B, 22° C	CY	5.74	27
	<i>m</i> -xylene	B, 22° C	CY	5.68	27
	2,3-dimethylbutane	B, 22° C	CY	5.52	27
	<i>p</i> -fluorotoluene	B, 22° C	CY	5.30	27
	toluene	B, 22° C	CY	5.22(a)	27
	toluene ^f	Neat, RT	—	5.80(b)	94
	<i>p</i> -chlorotoluene	B, 22° C	CY	5.20	27
	anisole	B, 22° C	CY	4.98	27
	ethyl benzene	(B ?), RT	TL(a)	5.70	26
<i>t</i> -butylbenzene	(B ?), RT	TL(a)	4.70	26	
benzhydrol	RT	TL(a)	7.62	68	
benzhydrol	B, RT	—	6.95	95	
isoborneol	B, RT	—	7.00	96	
Butyrophenone	cyclohexane	B, 25° C	II	5.60 ^h	97
	toluene	B, 25° C	II	5.38 ^h	97
	mesitylene	(B ?), RT	TL	6.08	26
	ethyl benzene	(B ?), RT	TL	5.84	26
	cumene	(B ?), RT	TL	5.82	26
	2,3-dimethylbutane	(B ?), RT	TL	5.32	26
<i>p</i> -(Trifluoromethyl)-acetophenone	<i>t</i> -butylbenzene	(B ?), RT	TL	4.86	26
	isopropanol	(2 <i>M</i> in B), RT	—	6.44	74

Table 8 (continued)

Ketone	Substrate	Conditions ^a	Compet. to ^{a, b}	log k^c	Ref.
<i>p</i> -(Trifluoromethyl)- benzophenone	isopropanol	(2 <i>M</i> in B),RT	—	6.34	74
<i>p</i> -Methylbenzophenone	isopropanol	(2 <i>M</i> in B),RT	—	5.93 ^d	74
4,4'-Dimethyl- benzophenone	isopropanol	(2 <i>M</i> in B),RT	—	5.83 ^d	74
Biacetyl	benzhydrol	B,RT	—	4.84	71
	benzhydrol	ACN,RT	—	5.11	71
	isopropanol	B,RT	—	3.52	71
	isopropanol	ACN,RT	—	4.11	71
	benzyl alcohol	B,RT	—	3.84	69
	methanol	B,RT	—	2.42	69
Cyclohexanone	isopropanol	γB,RT	—	6.26	98
Cyclopentanone	isopropanol	γB,RT	—	7.04	98
Pyruvic acid	isopropanol	Neat,RT	—	6.72	99
	<i>t</i> -butanol	Neat,RT	—	5.36	99
	methanol	B,RT	—	5.70	100
	2-butanol	B,RT	—	6.56	100
	benzyl alcohol	B,RT	—	7.15	100
Phenyl- <i>t</i> -butylketone	isopropanol	B,RT	—	4.38	101
(<i>p</i> -Methoxyphenyl)- <i>t</i> - butylketone	isopropanol	B,RT	—	3.54	101
9,10-Anthraquinone	isopropanol	B,RT	—	7.32	102

^a RT = room temperature; ACN = acetonitrile; B = benzene; W = water; CY = cyclohexane; TL = toluene; II = Type II photofragmentation; γB = γ-butyrolactone

^b Indicated when the rate constant given in the Table was obtained using competitive data from the original publication.

^c In units of $M^{-1} s^{-1}$.

^d See also Table 6.

^e See also Table 10.

^f See note in square brackets on page 89.

^g For a series of secondary alcohols see Table 11.

^h Obtained at high substrate concentration; in fact it should be considered as co-solvent.

ⁱ The value might be different from the one at "zero" isopropanol concentration, *i.e.* in non-polar solvent.

Zepp and Wagner¹⁰⁴ have recently examined the quenching of acetophenone triplets (benzene solvent, 25°C) by butylthiol and butylthiol- d_1 and found that quenching takes place with a rate constant of $\sim 1.4 \times 10^7 M^{-1} s^{-1}$. From a study of the isotopic dependence of the slopes of Stern-Volmer plots the authors conclude that hydrogen abstraction is not the main route for triplet removal from the system (see also ref. 105). Photolyses of γ-methoxy-butyrophenone/dodecyl-mercaptan mixtures lead to the trapping of the intermediate biradical which results from intramolecular hydrogen abstraction¹⁰⁶.

Becker¹⁰⁷ has examined the thermal and photochemical reactions of benzophenone with tri-phenylsilicon hydride and found evidence of hydrogen abstraction from the Si-H bond; however, neither quantum yields nor rate constants were determined.

The quenching of chloropentafluoroacetone singlets by germane has been recently examined by Yarwood (see Table 2)⁵⁷.

Gas phase studies have not been frequent. Kutschke¹⁰⁸ has attributed the quenching of perfluoroacetone phosphorescence ($k = 1.2 \times 10^8 M^{-1} s^{-1}$) by isobutane to hydrogen abstraction. O'Neal^{1,3} has examined the acetone-hydrogen bromide and the acetone-silane systems (see also Table 12 below).

A few studies have been concerned with steric effects in the photoreduction of aromatic ketones by alcohols.

Lewis¹⁰⁹ examined the effect of structural changes in the ketones moiety. Table 10 summarizes the kinetic data for isopropanol and 2,4-dimethyl-3-heptanol (quantum yields were also reported). The solvent is benzene and the concentration of substrate 2 *M*.

The photochemistry of *t*-butylphenyl ketone was also examined, and the results suggest that the reaction involves α -cleavage, rather than hydrogen abstraction, resulting in a rather complex mechanism (see also ref. 101). Since all the ketones examined have very similar triplet energies ($E_t = 73.4 \pm 1.0 \text{ kcal mol}^{-1}$) the author concludes that the decrease in reactivity is the result of increased steric

TABLE 9

PHOTOREDUCTIONS INVOLVING THE CLEAVAGE OF BONDS OTHER THAN C-H

Carbonyl compound	Substrate	Medium	Temp.	$k/M^{-1} s^{-1}$	Ref.
Acetone	SiH ₄	gas phase	25°C	2×10^6	3
Acetone	BrH	gas phase	25°C	6×10^8	1
Benzophenone	H ₂ O	neat	RT	5	43
Acetone	Bu ₃ SnH	<i>n</i> -hexane	RT	2×10^{8a}	54
Benzophenone	Bu ₃ SnH	benzene	RT	4.7×10^7	92
1-Naphthaldehyde	Bu ₃ SnH	benzene	RT	1.1×10^6	67
2-Acetonaphthone	Bu ₃ SnH	benzene	RT	2.0×10^6	67
Biacetyl	Bu ₃ SnH	benzene	RT	1.5×10^7	71
Biacetyl	C ₆ H ₅ OH	benzene	RT	3.4×10^{8b}	71
Biacetyl	C ₆ H ₅ OD	benzene	RT	1.0×10^{8b}	71

^a See ref. 72.

^b No chemical change detected, see text.

TABLE 10

STERIC EFFECTS IN THE PHOTOREDUCTION OF ALKYL ARYL KETONES^a

Ketone	$k_r(\text{iPrOH})^{b,c}$	$k_r(\text{C}_9\text{H}_{19}\text{OH})^b$
PhCOMe	7.5×10^5	2.8×10^5
PhCOEt	4.4×10^5	2.5×10^5
PhCO ^t Pr	1.3×10^5	6.6×10^5

^a Taken from ref. 95.

^b In $M^{-1} s^{-1}$, based on $k_q(\text{piperilene}) = 5 \times 10^9 M^{-1} s^{-1}$.

^c Another study (which also includes *t*-butyl phenyl ketone) by the same author has been recently published¹⁰¹.

hindrance. Comparison of the last two columns in Table 10 shows the effect of crowding around the reactive C-H bond. Pearson and Moss¹¹⁰ have studied this effect in the photoreduction of benzophenone by a series of secondary aliphatic alcohols and also found that steric effects can play an important role in determining the rate of reaction. The technique employed involved the measurement of the ratio of ketones produced when benzophenone was irradiated ($25 \pm 0.1^\circ\text{C}$) in a mixture of two alcohols*. Only relative reactivities were reported, these are given in Table 11. The last column gives the absolute rate constant, based on a rate of $1.25 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for isopropanol (see Table 8).

The kinetics of the hydrogen abstraction from benzene (by benzophenone triplets) has been examined by Dedinas *et al.*^{111, 112} using a flash technique and by Saltiel *et al.*⁹³ using phenyl radical trapping with carbon tetrachloride; the rates reported are $1.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $19 \text{ M}^{-1} \text{ s}^{-1}$ respectively. The quantum yield of phenyl radical formation⁹³ was about 0.002, in agreement with the upper limit of 0.05 (for benzophenone disappearance) previously reported by Beckett and Porter^{30, 94}.

The determination of activation energies requires either the direct measurement of the effect of hydrogen donors on the lifetime of triplet at different temperatures, or the study of the temperature dependence of the competition of reaction (2) with a process of known activation energy. In the latter case the temperature dependence of the most frequently employed competitive process, *i.e.* quenching by dienes, has not been measured, but a reasonable estimate can be obtained by graphical derivation of Debye's modified equation¹¹³⁻¹¹⁵. This type of approach has been used successfully in the case of Type II photofragmentations^{115, 116};

TABLE 11

STERIC EFFECTS IN THE PHOTOREDUCTION OF BENZOPHENONE BY SECONDARY ALCOHOLS

Substrate	Relative ^a reactivity	$k_r \times 10^{-6}/\text{M}^{-1} \text{ s}^{-1}$
Isopropanol	1.00	1.25 ^b
Cyclohexanol	1.60	2.00
Cyclopentanol	1.30	1.62
2-Octanol	1.05	1.31
2-Heptanol	1.00	1.25
Methyl- <i>t</i> -butylcarbinol	0.90	1.12
3-Heptanol	0.07	0.84
Methyl-isobutylcarbinol	0.39	0.49
Methyl-neopentylcarbinol	0.18	0.23
Di-isobutylcarbinol	0.074	0.09

^a Taken from ref. 110.

^b All the values are referred to this one, which in turn was taken from Table 8.

* The ketones are produced by transfer of a hydrogen atom from the substrate-derived ketyl radical to a ground state benzophenone molecule. This reaction frequently leads to quantum yields of benzophenone disappearance larger than unity (see Table 4).

TABLE 12
TEMPERATURE DEPENDENCE OF SOME PHOTOREDUCTIONS

Ketone	Substrate	Solvent or phase	E_a /kcal mol ⁻¹	log k^a	Ref.
Acetophenone	Isopropanol	Benzene	2.98	6.26	117
Acetone	Silane	Gas phase	3.4	6.3	3
Acetone	Hydrogen bromide	Gas phase	0.35 ^b	8.7	1

^a At 25°C in units of $M^{-1} s^{-1}$.

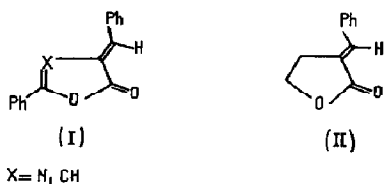
^b See the original publication for discussion of "best value" and error limit¹.

however, it has not been employed yet for any example involving intermolecular photoreduction. Table 12 summarizes the rather limited data available on temperature dependence of intermolecular hydrogen abstractions.

Miscellaneous

Rubin has examined the photoreduction of camphorquinone and benzophenone in toluene⁶³. From the amount of radicals which escape from the solvent cage, he concluded that at least in the latter system the radicals are likely to be produced with parallel spins, as could be expected from spin conservation.

A rather unusual example of wavelength dependence of the quantum yield has been reported in the photoreduction of lactones (I) and (II) in isopropanol^{118,119}. Rate constants were not measured; thus, it is difficult to establish whether the effect is also present in the elementary hydrogen abstraction step or whether the changes in quantum yield reflect changes in competitive reactions.



Wagner and Leavitt² have proposed that the photoreduction of α -trifluoroacetophenone by alkylbenzenes involves the formation of a charge transfer intermediate; however, Bryce-Smith *et al.*¹²⁰ have questioned whether charge transfer to α -trifluoroacetophenone follows, rather than precedes preliminary excitation.

In the photochemistry of the perfluoroacetone-propane system in the gas phase¹²¹ the mass balance of isopropyl radicals exceeded the yield of trifluoromethane, while the quantum yield of carbon monoxide formation decreased by addition of propane. The results were explained by a mechanism involving hydrogen abstraction by the ketone triplet.

Nakashima and Hayon⁴⁵ have examined the photochemistry of aqueous acetone-amide systems by flash photolysis. The reactions result in hydrogen

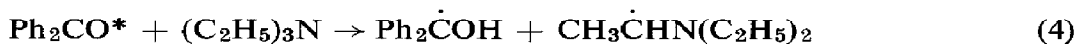
abstraction from C–H bonds (from formamide, *N,N*-dimethylformamide, acetamide, *N*-methylacetamide and *N,N*-dimethylacetamide). In the case of acetamide the presence of CH_3CONH radicals could not be established because its absorption is masked by the absorption by ground state acetone.

Dauben *et al.*¹²² have examined the photochemistry of 1,6-dimethylbicyclo [4.1.0] heptan-2-one in isopropanol solution. It yields 2,3,3-trimethylcyclohexanone, which in turn gives isopropyl-5,5-dimethylheptanoate. The primary process involves hydrogen abstraction from the solvent.

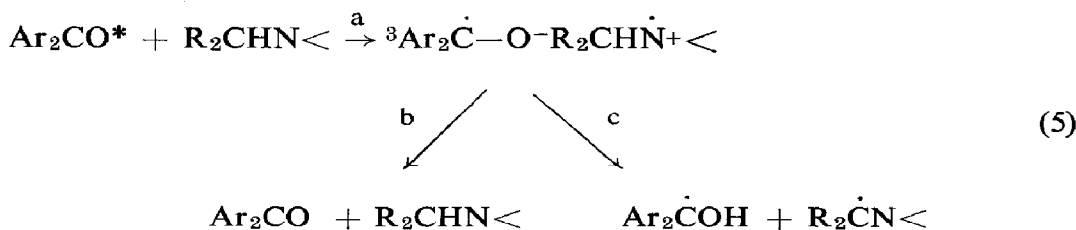
p-Aminobenzophenone abstracts hydrogen from paraffins but not from alcohols. This unusual result can be attributed to a low lying charge transfer state in the hydroxylic media^{10, 123}.

Processes involving charge transfer

Aromatic ketones can be photoreduced efficiently in the presence of molecules bearing the $>\text{CHN}<$ group¹²⁴. For the benzophenone–triethylamine system the overall process can be represented by:



i.e. from the point of view of the overall reaction there are no significant differences with the processes considered in the previous section; however, an analysis of rate and quantum yield data supports a rather more complex mechanism, involving charge-transfer^{124–132}:



The participation of charge-transfer (*CT*) interactions in these reactions is widely accepted nowadays. Davidson and Lambeth¹³³ have suggested that a triplet exciplex was the intermediate in the quenching of benzophenone triplets by triarylamines.

The main features of these reactions, which in turn have led to the proposal of the charge-transfer mechanism, can be summarized as follows: (a) the rate constants for these reactions (as measured by the rate of removal of triplets from the system) are much larger than could be expected for a triplet removal *via* radical-like abstraction of the most labile hydrogen atoms; for example, for benzophenone triplets the rate of abstraction from triethylamine is about 6000 times faster than from cyclohexane (12,000 on a *per* hydrogen basis), when the reactive C–H bonds are secondary in both cases (see Table 8)^{41, 89}; (b) the limiting quan-

tum yields of ketone consumption are lower than for abstraction from isopropanol, while the rate constants are larger. For example for benzophenone/2-butylamine the limiting quantum yield was only 1.12¹²⁹, while that for isopropanol $\Phi = 2.0$ ³⁰; (c) π, π^* triplets which are usually inefficient in photoreduction processes involving hydrocarbons or alcohols are photoreduced by amines. Typical examples are 2-naphthaldehyde¹³⁰, 2-acetonaphthone¹³⁰, *p*-aminobenzophenone¹²⁶ and fluorenone¹³⁴⁻¹³⁹; (d) the rates and quantum yields of the reactions are very dependent upon the polarity of the solvent. These can be regarded as *true* effects on the elementary step considered (see Table 13 below)*. Instead, in the benzophenone-isopropanol system the rate is independent of the concentration of the alcohol (using benzene as co-solvent)^{21, 89}, and even in 1:1 pyridine-water the rate suffers little change, if any¹²⁴; (e) evidence obtained by flash technique for the benzophenone/tri-*p*-tolylamine system shows a transient with absorption maxima at 670 nm¹⁴³. Davidson *et al.*^{143, 144} have suggested that this could be attributed to the cation, $(p\text{-CH}_3\text{C}_6\text{H}_5)_3\text{N}^+$. The evidence is based on a comparison of the spectrum obtained with those of other amine radical-cations¹⁴⁵.

The fact that the limiting quantum yield is lower than the theoretical value can be taken to mean that the chemical process is accompanied by "physical quenching". This means that for many of these systems the physical quenching by amines takes place with very high rate constants (frequently $k_q \geq 10^8 \text{ M}^{-1}\text{s}^{-1}$). The process cannot be energy transfer, at least in the case of aliphatic amines because the energetics would be unfavourable. In the case of the quenching of benzophenone triplets by aniline, diphenylamine and toluidines, Santhanam and Ramakrishnan¹⁴⁶ reported that there was no chemical reaction and suggested that energy transfer from triplet benzophenone to the amines takes place; however, their results (for diphenylamine) have been recently questioned by Pac *et al.*¹⁴⁷ who suggested a *CT* mechanism instead. It was also reported that the physical quenching is accompanied by chemical quenching as well¹⁴⁷. Moreover, the conclusion reached by Pac *et al.* is consistent with the fact that quenching by arylamines is also efficient in the case of low energy triplets such as fluorenone¹³⁴ and biacetyl⁷¹, where energy transfer would be very endothermic.

If amine quenching by energy transfer can be ignored, then the characteristics of the reaction [see (a) to (e) above] need to be explained by some type of strong interaction, and the proposal of a *CT* mechanism agrees with all the observations. This is also consistent with the trends of rate constants with the ionization potential of the amine. These have been closely examined by Cohen and Guttenplan^{148, 149} and will be discussed later.

* Solvent effects can be far more complicated, since they frequently involve changes in the yields of intersystem crossing (*e.g.* fluorenone and *p*-aminobenzophenone)^{140, 141} or changes in the relative positions of n, π^* and π, π^* triplets^{18, 20-22, 142}.

The production of ketyl radicals in the photoreduction of ketones by amines has been confirmed by electron spin resonance. Davidson and Wilson¹³⁹ report an e.s.r. study of the photoreduction of fluorenone and benzophenone.

Table 13 exemplifies the effect of solvent polarity on these reactions. The rate constants correspond to "both" processes, *i.e.* to k_{5a} . Some of the examples do not result in photoreduction, a fact that can be taken to mean that $k_{5b} \gg k_{5c}$.

Cohen and Chao¹²⁹ have also examined the effects of concentration on the relative rates of photoreduction of benzophenone triplets by several amines.

CT mechanisms have also been proposed in the Type II photoelimination reactions of α -aminoacetophenones¹⁵⁰.

Table 14 summarizes some of the rate constants available in the literature. These can be correlated with ionization potential, electron affinities and triplet energies^{148, 149}; these correlations are discussed in a later section.

TABLE 13

SOLVENT EFFECTS IN THE INTERACTION OF CARBONYL TRIPLETS WITH AMINES

Carbonyl compound	Amine	Solvent	k_{5a}^a	ϕ_{lim}	Ref.
Benzophenone	2-butylamine	benzene	2.3×10^8	1.12	124
		acetonitrile	3.8×10^8	1.04	124
2-Naphthaldehyde	triethylamine	0.02 <i>N</i> NaOH in 1:1 pyridine-H ₂ O	1.7×10^7	0.77	124
		acetonitrile	8×10^6	1.20	130
		t-butanol	—	0.63	130
		benzene	5×10^5	0.46	130
2-Acetonaphthone	triethylamine	acetonitrile	6×10^5	0.67	130
		t-butanol	—	0.16	130
		benzene	1×10^5	0.05	130
Biacetyl	triethylamine	benzene	5.0×10^7	—	71
		acetonitrile	2.7×10^8	—	71
Biacetyl	aniline	benzene	5.0×10^8	~0	71
		acetonitrile	1.5×10^9	~0	71

^a In units of $M^{-1} s^{-1}$.

TABLE 14

RATE CONSTANTS FOR TRIPLET QUENCHING BY AMINES

Ketone	Substrate	Solvent	k_q^a	Ref.
Benzophenone	Triethylamine	Benzene	2.3×10^9	89
	<i>N</i> -methyl-2-butylamine	Benzene	1.4×10^9	89
	2-Butylamine	Benzene	2.5×10^8	96, 124
	<i>N,N</i> -dimethylaniline	Benzene	2.7×10^9	89
	Triphenylamine	Benzene	7.6×10^8	143
	Triphenylamine	Acetonitrile	1.4×10^{10}	143
	Tri- <i>p</i> -tolylamine	Benzene	8.4×10^9	143
	Diphenylamine	Acetonitrile	4×10^9	147

Table 14 (continued)

Ketone	Substrate	Solvent	k_d^a	Ref.	
Butyrophenone ^b	Trimethylamine	Benzene	1.3×10^9	153	
	Triethylamine	Benzene	6.5×10^8	153	
	Diethylamine	Benzene	9.7×10^8	153	
2-Naphthaldehyde	Dimethylamine	Benzene	6×10^8	153	
	Triethylamine	Benzene	5×10^5	130	
2-Acetonaphthone	Triethylamine	Benzene	1×10^5	130	
Valerophenone	Triethylamine	Benzene	4.2×10^9	151	
<i>p</i> -Aminobenzophenone	Triethylamine	Cyclohexane	5.4×10^7	152	
Biacetyl ^c	Triethylamine	Benzene	5×10^7	71	
	Isopropylamine	Benzene	2.8×10^7	71	
	Isopropylamine-d ₂	Benzene	2.4×10^7	71	
	Diethylamine	Benzene	2.2×10^7	71	
	Diethylamine-d ₁	Benzene	2.4×10^7	71	
	Tri- <i>n</i> -propylamine	Benzene	8.0×10^7	71	
	Aniline	Benzene	5.0×10^8	71	
	Aniline-d ₂	Benzene	9.6×10^8	71	
	Diphenylamine	Benzene	1.7×10^9	71	
	Triphenylamine	Benzene	3.1×10^7	71	
	<i>N,N</i> -dimethylaniline	Benzene	2.7×10^8	71	
	<i>N,N</i> -dimethylaniline	Benzene	8.4×10^8	71	
	Biacetyl ^{c, d}	Diethylamine ^e	Gas phase	$\sim 6 \times 10^5$	153
		Dimethylamine ^e	Gas phase	$\sim 3 \times 10^5$	153
		Triethylamine	Gas phase	$\leq 8 \times 10^4$	153
Fluorenone	Triethylamine	Cyclohexane	3.2×10^7	137	
	<i>N,N</i> -dimethylaniline	Benzene	6.0×10^8	136	
	<i>N,N</i> -dimethylaniline	Hexane	2.5×10^9	134	
	2-Butylamine	Benzene	5×10^9	149	
	<i>N</i> -methyl-2-butylamine	Benzene	2.9×10^7	149	
	<i>p</i> -Chlorodimethylaniline	Benzene	2.8×10^8	136	
	Aniline	Hexane	1.8×10^9	134	
	Triethylamine	Hexane	2×10^8	134	
	Diethylamine	Hexane	1.4×10^7	134	
	Acetone	Trimethylamine	Gas phase	8.8×10^6	153
Triethylamine		Gas phase	2.5×10^7	153	
Diethylamine ^e		Gas phase	$\sim 2.5 \times 10^7$	153	
Dimethylamine ^e		Gas phase	2.5×10^7	153	

^a At room temperature, unless otherwise indicated. In units of $M^{-1} s^{-1}$.

^b Measured in competition with the Type II process, using k (Type II) = $8 \times 10^6 s^{-1}$.

^c From phosphorescence measurements.

^d Using τ (triplet) = $1.8 \times 10^{-3} s$.

^e A contribution from abstraction from the N-H bond is possible.

^f At 100°C, using τ (triplet) = $9 \times 10^{-5} s$.

Turro and Engel⁷¹ have examined in detail the quenching, the fluorescent and phosphorescent emissions from biacetyl by a variety of substrates in various solvents. Some of their data (for phosphorescence quenching) have been included in Tables 13 and 14. The singlet state of biacetyl has also been shown to be quenched by amines^{71, 133, 154}.

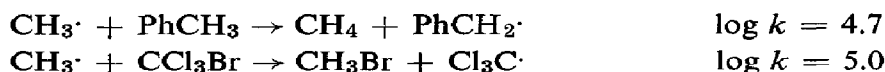
In the gas phase the triplet states of acetone and biacetyl are quenched with a smaller rate constant than in solution¹⁵³. In the case of acetone the rate constants agree well with calculated values obtained using a radical-like model (see below); therefore, it seems likely that in the gas phase these reactions must be considered as radical-like, rather than charge-transfer processes.

Neither steric, nor temperature effects seem to have been examined for these reactions.

Not only amines, but also sulphides^{96, 148}, phosphines^{133, 155, 156}, phosphites¹³³, arsines¹⁵⁶, stibines¹⁵⁶ and bismuthines¹⁵⁶ quench the triplet state of ketones. Some of these systems are discussed next.

ATTACK AT MULTIVALENT CENTRES (S_H2 REACTIONS)

Most free radicals are capable of abstracting a terminal atom from a molecule. The abstracted atom quite frequently is hydrogen or a halogen, *e.g.*^{157, 158}:



with both rate constants in the gas phase at 25°C and in units of $M^{-1}\text{s}^{-1}$. A similar process can take place at a multivalent centre^{8, 159}:



where $\text{X}\cdot$ is a free radical and MR_n an organometallic compound. Ingold and Roberts¹⁵⁹ have compiled the information which was available on this type of reaction until mid-1970. Alkoxy radicals are among the radicals which can bring about the S_H2 displacement of reaction (6). Known examples include elements of groups I, II, III, IV, and V^{5, 8, 160, 161}.

Since alkoxy radicals and ketone triplets are known to show analogous behaviour (see above) one can expect reaction (7) to occur:

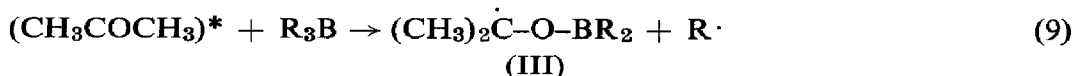


The first evidence that this reaction could take place was reported by Grotewold and Lissi in 1968 when they showed that triethylborane quenched the phosphorescence from biacetyl (in the gas phase) and suggested that chemical quenching could be involved^{162, 163}. In another report from the same laboratory¹⁶⁴, evidence was obtained suggesting that reaction (8) was responsible for the triplet quenching.



The first studies were all centred on organoboron compounds. Acetone triplets were shown to bring about a similar displacement at the boron centre in several organoboranes in solution^{4, 165} as well as in triethylborane in the gas

phase¹⁶⁶. The studies in solution allowed the identification of the co-radical (III) by electron spin resonance:



definitely establishing the course of reaction. Typically, the e.s.r. spectra of (III) show no coupling from the protons in R, a boron (nuclear spin = 3/2) coupling of 8–9 G and for the methyl protons $a_{\text{H}} = 20.6 \text{ G}^4$. A similar behaviour was observed with other aliphatic ketones, and in some cases (in all cases in the gas phase) reaction (7) could be observed in competition with the Norrish Type I fragmentation:



Table 15 shows a summary of rate constants for the reaction of acetone triplets with several organoboranes. The values for t-butoxy radicals are also given.

The reaction seems to be sterically controlled, a feature which is common to many free radical organometallic reactions. This aspect of the reaction is discussed in the next section.

The reaction of aromatic ketones with organoboranes was recently examined¹⁶⁷; the interaction between the carbonyl triplet and the organoborane results in the formation of similar products to those of the reactions of alkanones. However, the reactions are significantly faster, with rate constants around or over $10^8 \text{ M}^{-1} \text{ s}^{-1}$ for ketones having either n,π^* or π,π^* low lying triplets; the quantum yields were always below Φ_{isc} , the quantum yield of intersystem crossing. From an analysis of the results a mechanism involving an intermediate was proposed:

TABLE 15

RATE CONSTANTS FOR THE $\text{S}_{\text{H}2}$ REACTION OF ACETONE TRIPLETS AND OF T-BUTOXY RADICALS WITH ORGANOBORANES AT 20° C

R_3B	Me_2CO^* $k_9(\text{M}^{-1} \text{ s}^{-1})$	^tBuO $k_6(\text{M}^{-1} \text{ s}^{-1})$
Pr_3B	$1.4 \times 10^{7\text{a}}$	—
$(\text{C}_6\text{H}_{13})_3\text{B}$	$8 \times 10^{6\text{a}}$	—
$^n\text{Bu}_3\text{B}$	$7 \times 10^{6\text{a}}$	$3 \times 10^{7\text{b}}$
$^i\text{Bu}_3\text{B}$	$8 \times 10^{4\text{a}}$	$1 \times 10^{6\text{b}}$
$^s\text{Bu}_3\text{B}$	$\leq 10^{4\text{a}}$	$2 \times 10^{5\text{b}}$
$\text{Et}_3\text{B}^{\text{c}}$	$1 \times 10^{8\text{d}}$	$1 \times 10^{7\text{e}}$

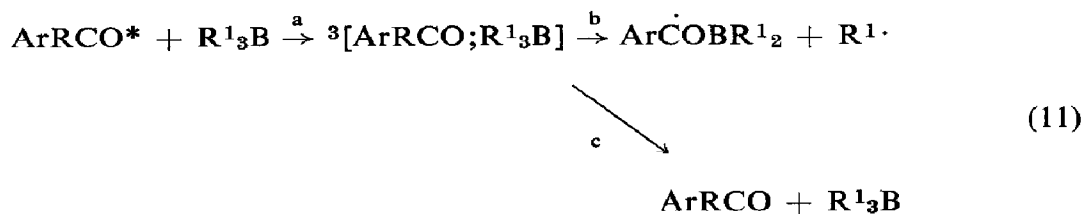
^a Ref. 4.

^b Ref. 161.

^c In the gas phase.

^d Ref. 166.

^e Ref. 160, at 134.5° C.

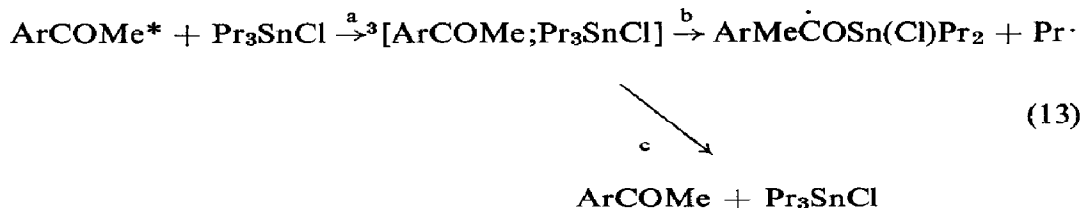


The limiting quantum yield can therefore be interpreted as:

$$\lim_{[\text{R}^1_3\text{B}] \rightarrow \infty} (\Phi_{-K}) = \Phi_{\text{isc}} \frac{k_{11\text{b}}}{k_{11\text{b}} + k_{11\text{c}}} \quad (12)$$

Table 16 shows the values of $k_{11\text{a}}$ for a variety of reactions in benzene solvent.

Tri-*n*-propyltin chloride has been shown to photoreduce acetophenone and *p*-methylacetophenone in a similar manner^{5,168}:



$S_{\text{H}2}$ reactions involving the attack of metallic centres by excited species are probably more general than suggested by the examples showed herein. With the only exception of the example of reaction (13), all the other systems examined involve the attack at boron; however, other metallic centres are likely to be equally reactive.

TABLE 16

KINETIC AND QUANTUM YIELD DATA FOR THE REACTION OF AROMATIC KETONES WITH ORGANO-BORANES AND ORGANOTIN COMPOUNDS (28°C)

Ketone	Substrate	log k	$\Phi_{11\text{m}}/\Phi_{1\text{sc}}$	Ref.
Acetophenone (ACP)	ⁿ Bu ₃ B	8.30	0.62	167
ACP	¹ Bu ₃ B	7.55	0.26	167
ACP	^s Bu ₃ B	6.70	0.29	167
<i>p</i> -methyl-ACP	ⁿ Bu ₃ B	8.70	0.48	167
<i>m</i> -methoxy-ACP	ⁿ Bu ₃ B	8.80	0.70	167
<i>p</i> -methoxy-ACP	ⁿ Bu ₃ B	8.80	0.50	167
<i>p</i> -phenyl-ACP	ⁿ Bu ₃ B	8.50	0.50	167
Benzophenone	ⁿ Bu ₃ B	7.65	—	167
Propiophenone	ⁿ Bu ₃ B	7.78	—	167
<i>p</i> -Cyano-ACP	ⁿ Bu ₃ B	8.75	—	167
ACP	ⁿ Pr ₃ SnCl	8.60	0.13	168
<i>p</i> -Methyl-ACP	ⁿ Pr ₃ SnCl	8.35	0.13	168

Solvent effects have been examined in the photoreduction of acetophenone by tri-*n*-butylborane in benzene/*t*-butanol mixtures at room temperature¹⁶⁷. It was concluded that increasing solvent polarity results in a decrease of k_{11b}/k_{11c} and an enhancement of k_{11a} . The latter would be consistent with (a) an enhancement of the reactivity due to an increase in π, π^* character, and (b) stabilization of the intermediate triplet exciplex due to solvation.

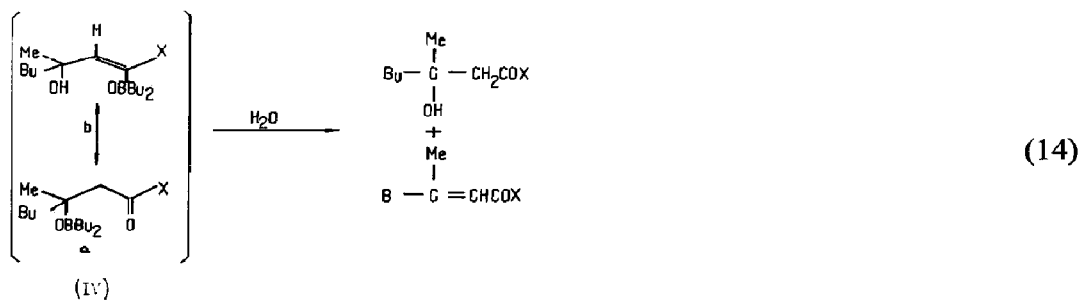
It is interesting to note that acetone is some 30–50 times less reactive than aromatic ketones in S_H2 reactions at the boron centre. In the case of acetone with organotin compounds no radicals could be detected by e.s.r.¹⁶⁸. (This puts an upper limit of $\sim 2 \times 10^4 M^{-1} s^{-1}$ to the rate constant.) This is surprising, since from a comparison of triplet energies, steric hindrance and radical-like character one would expect acetone to be more reactive; this is not the case. Certainly there are other relevant factors, and the results suggest that the formation of the intermediate triplet exciplex is favoured by the presence of an aromatic ring in the ketone moiety, and this may even be a necessary condition for the formation of the intermediate^{167,168}.

Experiments attempting to observe an S_H2 displacement at boron using perfluoroacetone triplets have failed, both in solution⁴ and in the gas phase. In the latter attempt the evidence pointed to a hydrogen abstraction process¹²¹.

Miscellaneous

A process similar to that of reaction (7) is presumably involved in the initiation of the photochemical 1,4-addition of β -unsaturated carbonyl compounds to organoboranes^{4,169–171}.

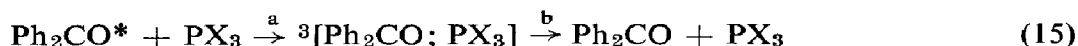
The photochemical reaction of acetylacetone with tri-*n*-butylborane has been recently examined by Utimoto *et al.*¹⁷². The authors propose a mechanism involving the enol of the diketone and leading to (IV), which in turn leads to the ultimate products. An alternative mechanism, also consistent with experiment would involve an S_H2 displacement by the excited carbonyl group, leading to (IVb) by cross-combination of the radicals.



One aspect of these reactions which deserves further comment is the similarity with the quenching by phosphorous compounds. Davidson and Lambeth¹³³ found that triphenylphosphine and trimethylphosphite are quenchers of benzo-

phenone triplets. The technique employed involved the competition between the quenching by the phosphorous compound (k_q) and the photoreduction of benzophenone triplets by benzhydrol (k_r). The data are summarized in Table 17. The last column has been calculated assuming $k_r = 9 \times 10^6 M^{-1} s^{-1}$ and independent of the solvent (see Table 8).

The quenching process could be understood as analogous to reaction (11), *i.e.*,



where k_{15b} would be large enough as to preclude the occurrence of alternative processes which could result in chemical change. In fact Wescott *et al.*¹⁵⁵ have shown that some photodeoxygenation takes place (leading to OPPh_3); however, the quantum yield is likely to be very low*.

The interaction of butyrophenone triplets with several group V organometallics (see Table 17) has been examined in competition with the Type II process¹⁵⁶. All the rate constants are close to diffusion controlled and they do not follow an increasing trend with decreasing ionization potential of the substrate¹⁷⁹. The quantum yields of "chemical change" are very small with the only exception of triphenylbismuthine whose quenching leads to the formation of phenyl radicals which can be trapped by carbon tetrachloride.

This analogy (see reaction 15) can probably be extended to other systems, suggesting that processes which are sometimes considered as essentially different can in fact involve similar interactions at a molecular level.

TABLE 17

INTERACTION OF GROUP V ORGANOMETALLICS WITH KETONE TRIPLETS

Ketone	Substrate	Solvent	k_q/k_r	$k_q/M^{-1} s^{-1}$	Ref.
Benzophenone ^a	Ph_3P	benzene	40	3.60×10^8	133
Benzophenone ^a	Ph_3P	acetonitrile	35	3.15×10^8	133
Benzophenone ^a	$(\text{MeO})_3\text{P}$	benzene	26	2.35×10^8	133
Benzophenone ^a	$(\text{MeO})_3\text{P}$	acetonitrile	29	2.60×10^8	133
Butyrophenone ^b	Ph_3P	benzene	—	1.8×10^9	156
Butyrophenone ^b	Ph_3As	benzene	—	8.4×10^8	156
Butyrophenone ^b	Ph_3Sb	benzene	—	2.8×10^9	156
Butyrophenone ^b	Ph_3Bi	CCl_4	—	1.0×10^{10}	156

* Measured in competition with the photoreduction by benzhydrol, see text.

^b The measurements were competitive to the Type II process, taking the rate constant for intramolecular abstraction as $8 \times 10^6 s^{-1}$.

* A similar process involving the interaction of *t*-butoxy radicals with organophosphorus compounds is well known, and the intermediates have been characterized by electron spin resonance spectroscopy¹⁷³⁻¹⁷⁸.

Triphenylphosphine has also been shown to quench the fluorescence of biacetyl, fluorenone and anthracene¹³³. In general the quenching is less efficient and less solvent dependent than the analogous reaction by triphenylamine.

CORRELATIONS AND SEMI-EMPIRICAL MODELS

The correlations and semi-empirical models discussed in this section apply to some of the examples already discussed above.

The final aim of any reaction model is to obtain the complete potential energy surface for the reaction under study on purely theoretical grounds. This is, of course, an optimistic aim and we usually have to content ourselves with methods which can predict kinetic data from other experimental parameters; these can be kinetic or non-kinetic in origin. The former are called correlations.

Walling and Gibian²⁷ have applied Hammett's correlation to the reaction of substituted toluenes with benzophenone triplets in benzene and obtained a good correlation with $\rho = -1.16$. Some of the data used have already been included in Tables 4 and 8.

Four different models have been reported, aiming to estimate, correlate or predict trends in rate constants; these are discussed below.

Suppan⁸² has proposed a model based on electrostatic interaction and on the energy needed to localize the excitation on the carbonyl function. According to this model, the activation energy is calculated as:

$$E_a = E_{es} + E_L^* \quad (16)$$

where E_{es} can be evaluated as:

$$E_{es} = \delta_q \cdot \Delta_q / r_0 \quad (17)$$

$$\begin{array}{c} \delta^+ \quad \delta^- \quad \Delta^- \\ >C=O \cdots H-R \end{array}$$

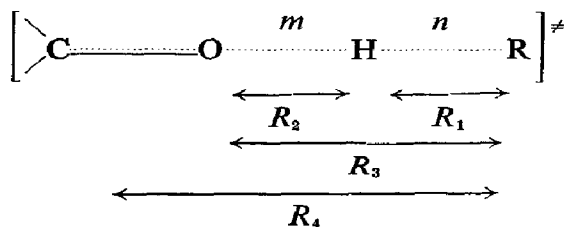
E_L^* is the energy necessary to localize the antibonding electron on the carbonyl function. For n, π^* states $E_L^* = 0$. We note here the similarity between this model and the assumption (mentioned earlier) that in the case of π, π^* triplets the reaction proceeds from a thermally equilibrated n, π^* state; both predict an exponential temperature dependence with the energy gap.

Suppan's model does not take into account the energetics of the reaction; therefore, it cannot predict or correlate the changes in rate constants which result from changes in the thermochemistry of the reaction. If all other parameters are constant, it predicts the changes in reactivities expected from changes in electrostatic interaction. This type of effect has been observed in heteroaromatic ketones⁷⁸⁻⁸⁰. The report by Suppan⁸² includes a comparison of experimental and calculated parameters, and plots showing the expected effect of different substituents on the rates of abstraction.

Heller¹⁸⁰ has proposed that photoreductions can be interpreted as a special form of radiationless transition, where the R–H bond to be cleaved behaves as an acceptor of the vibrational energy resulting from electronic–vibrational relaxation. The assumption that this type of interaction can lead to hydrogen transfer in these systems has been seriously questioned^{91,181*}.

A reaction model based on the bond energy–bond order (BEBO) method has been recently proposed^{72,181}. It is aimed to calculate activation energies and pre-exponential factors for *radical-like* atom abstractions^{183–187}.

In this model the transition state is considered to have a structure of the type:



where m and n are bond orders which add to one and R_1 to R_4 distances.

The reaction coordinate is determined by all the structures for which:

$$m + n = 1 \quad (18)$$

and for these structures the potential energy is given by:

$$V = E_1 - E_1 n^p - E_2 m^q - (E_t - E_a)m + V_{\text{rep}} + V_{\text{rep}'} \quad (19)$$

where E_1 and E_2 are the stable bond dissociation energies for the R–H and O–H bonds respectively, p and q are Pauling's bond indices, E_t is the triplet energy, E_a the double bond contribution to the C=O bond, and V_{rep} and $V_{\text{rep}'}$ are anti-morse functions according to Sato's expression¹⁸⁸ and take into account the repulsive interactions among the electrons involved; in general, $V_{\text{rep}'} \sim 0.1 V_{\text{rep}}$. Figure 1 shows the role of the different terms in eqn. (19) in determining the shape of the potential energy profile.

The method can be combined with a suitable version of transition state theory (the local bond properties treatment is usually employed)¹⁸³ in order to obtain the pre-exponential factors.

It should be noted that, given a certain substrate, the kinetic parameters will be determined by the factor $E_t - E_a$. If the lowest triplet is n, π^* in character this is the only property of the carbonyl compound which is important for the calcula-

* Wagner⁷⁵ has examined the possibility of explaining the high yield of radiationless decay which accompanies the singlet Type II photofragmentation using this type of interaction. Turro¹⁸² has proposed that the interaction with the γ -hydrogens in α -cyclopropoxy acetophenone acts as an energy sink, being therefore responsible for the large yield as radiationless decay.

tions. This is a fact which has very important practical implications, since it allows the easy tabulation of pre-calculated kinetic parameters. Figure 2 shows several curves which allow the evaluation of activation energies for the abstraction of hydrogen atoms *bonded to carbon* given the parameter $E_t - E_d$ and the bond energy⁷². Similar information on pre-exponential factors and structural parameters of the transition state has been reported⁷². The model is only applicable to n, π^* states.

Further simplification of the method can be achieved by assuming the pre-exponential factors to be proportional to the number of equivalent reactive hydro-

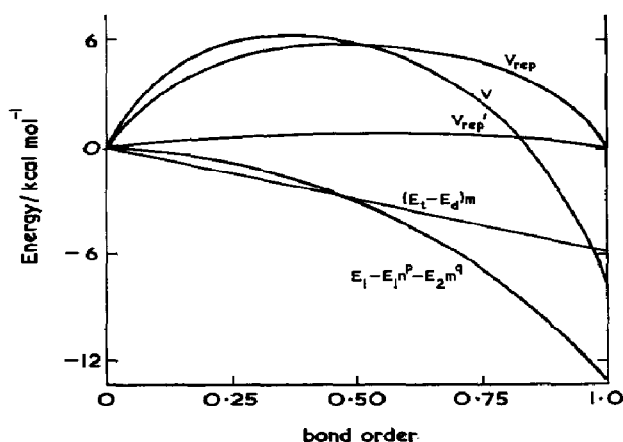


Fig. 1. Role of the different parameters in eqn. (19) in determining the potential energy profile for the reaction of benzophenone triplets with a C-H bond with $E_1 = 91 \text{ kcal mol}^{-1}$. (Reproduced by permission from *J. C. S. Perkin Trans. II*, (1972) 1667.)

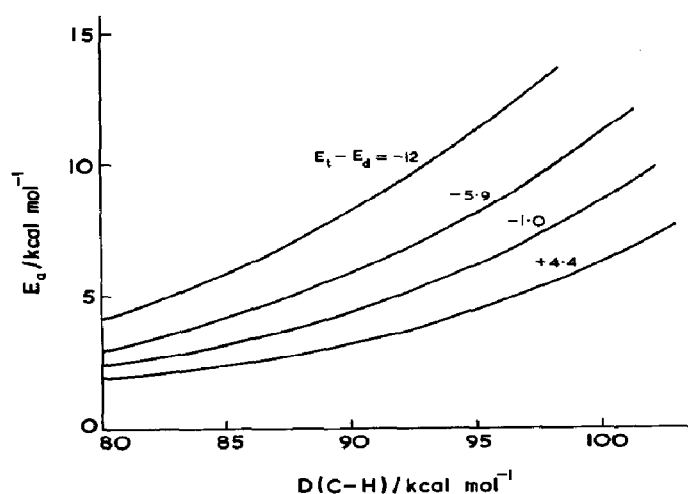


Fig. 2. Calculated activation energies for several values of $(E_t - E_d)$. (Reproduced by permission from *J. C. S. Perkin Trans. II*, (1972) 1672.)

gen atoms and independent of other parameters¹⁸⁹. Then, the relative rates of abstraction for substrates 1 and 2 can be calculated using eqn. (20), which has proved useful in a variety of examples¹⁸⁹.

$$\frac{k_1}{k_2} = \frac{\exp(E_{a1}/RT) \times (\text{no. H})_1}{\exp(E_{a2}/RT) \times (\text{no. H})_2} \quad (20)$$

In general, the parameters obtained using the method seem to be valid in solution, particularly in non-polar solvents, as well as in the gas phase; however, special care is recommended when the calculated activation energy is very low, particularly if it is lower than the formal activation energy for diffusion through the solvent.

The method has also been applied to a variety of reactions which involve the cleavage of bonds other than C-H¹⁹⁰. As pointed out in the previous section (see Table 9), only a few examples of reactions of this type have been examined. The reactions of triplet acetone with hydrogen bromide and silane have been studied by O'Neal and coworkers in the gas phase^{1,3}. The calculated kinetic expressions compare well with the experimental values^{181,190}.

The application of the modified BEBO method to the reaction of triplet carbonyl compounds with tin-hydrogen bonds shows a reasonably good agreement with experiment. For example, for the benzophenone-tributyltin hydride system in benzene, Davidson *et al.*⁹² determined a rate constant of $4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at room temperature. The calculated value for this system is $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (ref. 72) using $\beta = 2.04 \text{ \AA}^{-1}$ (the Morse parameter).

Of particular interest are the results of the calculations for hydroxylic compounds. The calculations suggest that the cleavage of O-H bonds should be possible in some systems, particularly for ketones having high triplet energies and where an inversion of states is unlikely to occur. Since the photoreduction of ketones by alcohols is a well known reaction, one wonders whether the production of alkoxy radicals could have remained unobserved; it is certain that in electron spin resonance studies this could easily be the case, since alkoxy radicals are not usually observed in solution. Another factor which should be taken into account is that the reaction which alkoxy radicals are most likely to undergo is hydrogen abstraction, a process which would mask the actual behaviour of the carbonyl triplet. In addition, the rate of production of alkoxy radicals will always be smaller than that of production of ketyl radicals, while the lifetime of the latter will probably be longer. As a result of this the steady state concentration of ketyl radicals will usually be several times larger than that of alkoxy radicals. The conclusion of this reviewer is that although the cleavage of O-H bonds cannot be proved by the arguments presented herein, at least it is certain that this is a possible reaction and that the frequent assumption that the reaction does not take place lacks experimental and theoretical support. This conclusion is further supported by the recent investigation of the photochemistry of aromatic ketones in aqueous solution by

Ledger and Porter⁵⁷ and by the quenching of the phosphorescence from biacetyl by phenols observed by Turro and Engel⁷¹.

Table 18 shows a series of calculated parameters, which in some cases can be compared with the data in Tables 8 and 9.

Dougherty¹⁹¹ has reported a perturbation molecular orbital treatment for several kinds of photochemical reactions. The application of the BEBO method to reaction (2) is consistent with this treatment and involves the assumption of a particular barrier shape for the group of N-type reactions considered.

Finally, we note that the modified BEBO method cannot be used to predict substituent effects, steric effects or changes in reactivities resulting from changes in the nature of the excited states⁷².

Guttenplan and Cohen^{148,149} have recently proposed a correlation which applies to reactions which occur by *CT* mechanisms (see above) and is based on a free energy relationship previously reported by Weller *et al.*¹⁹¹⁻¹⁹³.

The authors propose the following equation^{148,149}:

$$\Delta G^\ddagger \sim -E_t + IP_D - E(A^-/A) + C \quad (21)$$

where E_t is the triplet energy, IP_D the ionization potential of the donor, $E(A^-/A)$ the reduction potential of the ketone and C a constant. For a series of donors reacting with the same acceptor eqn. (21) reduces to:

$$\Delta G^\ddagger \sim IP_D + \text{constant} \quad (22)$$

while for a series of acceptors with the same donor,

$$\Delta G^\ddagger \sim -E_t - E(A^-/A) + \text{constant}' \quad (23)$$

Equation (22) has been applied to benzophenone¹⁴⁸ and fluorenone¹⁴⁹, while eqn. (23) has been used with triethylamine as the donor¹⁴⁹.

TABLE 18

KINETIC PARAMETERS OBTAINED USING THE MODIFIED BEBO METHOD¹⁵⁷ (IN THE GAS PHASE, 25°C)

Ketone	Substrate	$E_a/\text{kcal mol}^{-1}$	$\log k^a$	Ref.
Acetone	hydrogen bromide	0.37	9.2	181
Acetone	silane	2.5	7.0	181, 190
Acetone	germane	2.6	6.3	190
Acetone	ammonia	6.2	6.0	190
Benzophenone	ammonia	11.5	1.4	190
Benzophenone	hydrazine	1.8	7.6	190
Benzophenone	ROH	7.6	3.5	190
Acetophenone	isopropanol	3.7	5.7	72
Benzophenone	isopropanol	5.0	5.4	72
Benzophenone	cyclohexane	7.6	5.3	72
Benzophenone	tetrabutyltin	7.6	5.2	72
Benzophenone	tributylstannate	1.1	7.5	72, 190
Benzophenone	toluene	4.2	6.1	72

^a k in units of $M^{-1} s^{-1}$.

It was found that the slopes and intercepts of the $\log k$ vs. IP_D plots were dependent on the nature of the substrates, *i.e.* for benzophenone in benzene:

$$\log k = 21.80 - 1.55 IP_D \text{ (for aliphatics)}^{148} \quad (24)$$

$$\log k = 27.25 - 2.42 IP_D \text{ (for aromatics)}^{148} \quad (25)$$

(with k in $M^{-1} s^{-1}$ and IP_D in eV).

From an examination of these slopes and intercepts it was concluded that the interactions of benzophenone triplets with electron donors involve only partial transfer of charge¹⁴⁸. "Mixing" with partial transfer of the α -hydrogen atom was also proposed.

Earlier it was pointed out that mixed interactions could be expected, and that the examples usually considered as radical-like and *CT* mechanisms merely represent opposite ends in a wide range of mixed interactions. It is therefore interesting to compare the predictions using both models.

The radical-like (*RL*) model can be conveniently expressed using the modified BEBO method¹⁸¹.

Surprisingly, there is a group of substrates for which both methods agree reasonably well with experiment, even when the type of interactions taken into account are substantially different^{72, 148, 149}.

The comparison has been carried out for benzophenone. The choice reflects the availability of experimental data, as well as the fact that the lowest triplet has n, π^* character.

We note that neither method can predict the mechanism of reaction. They can only predict and/or correlate a rate constant assuming that a certain type of interaction is involved. In other words, they will not predict whether an alternative reaction path will be fast enough to "take-over"; however, one would expect the failures of either method to be associated with the prediction of a low rate constant, but not a high one.

Table 19 shows a comparison of calculated (by both methods) and experimental data. IP_D and the bond dissociation energy of the weakest bond to hydrogen are also given. The possibility of contributions from abstractions from bonds other than the weakest one has not been taken into account.

An examination of the data for substrates 1, 2 and 3, which can be regarded as typical *CT* examples clearly show that radical-like calculations using the BEBO method result in an underestimation of the rate constant. In the case of aliphatic hydrocarbons (nos. 8 and 9), which could hardly be considered as electron donors, *RL* predictions are much closer to the experimental value. For the group of compounds having aromatic rings (but excluding benzene) both methods predict the right order of magnitude; however, the *RL* method seems to predict more accurately the trends, and in particular, it predicts successfully a large fall in reactivity from cumene to *t*-butylbenzene (the failure of the *CT* model could be attributed to the impossibility of interactions with the α -hydrogens). In the case of compounds

TABLE 19

COMPARISON OF CALCULATED AND EXPERIMENTAL RATE CONSTANTS FOR THE INTERACTION OF BENZOPHENONE WITH VARIOUS SUBSTRATES

No.	Substrate	IP_D/eV^a	$D(RH)^b$	$\log k$			Ref.	
				CT	eqn. ^c RL	Exp.		
1	Triethylamine	7.50	94	10.20	24	4.95	9.36	89
2	2-Butylamine	8.70	91	8.30	24	4.95	8.40	96
3	Di-n-butylsulphide	8.30	94	8.90	24	4.75	8.93	148
4	Di-n-propyl ether	(9.50)	91	(7.10) ^d	24	5.60	6.97	197
5	<i>p</i> -Dioxane	9.13	91	7.65	24	4.97	5.63	41, 72
6	2-Propanol	10.15	83	6.10	24	5.01	6.10	21, 30
7	Ethanol	10.50	91	5.50	24	5.27	5.75	41
8	Cyclohexane	9.88	94	6.50	24	5.33	5.56	41, 72, 91
9	2,3-Dimethylbutane	10.02	91	6.25	24	5.27	5.52	27
10	Benzene	9.25	110	4.25	25	0	4.25	83
11	Toluene ^e	8.82	85	5.90	25	~6.07	5.80	94
12	Ethyl benzene ^e	8.76	82	6.05	25	6.24	6.20	26, 94
13	Cumene ^e	8.48	79	6.80	25	6.17	6.17	27, 94
14	<i>t</i> -Butylbenzene ^e	8.68	97	6.25	25	4.45	5.01	26, 94
15	<i>p</i> -Xylene	8.44	85	6.75	25	6.37	6.45	27, 94
16	Tetrabutyltin	(8.20)	94	(9.10)	24	5.16	5.85	92
17	Tributylstannate	—	70	—	24	7.52	7.68	92

^a See refs. 179, 195 and 196.^b In units of kcal mol⁻¹.^c Equation used to calculate the rate constant according to the CT model.^d Watanabe¹⁹¹ reports a value of 9.27 eV for the ionization potential; using this value $\log k = 7.42$.^e The value for toluene from Table 8 with subscript b has been preferred in order to be consistent with Guttenplan and Cohen's work¹⁴⁸. All the rate constants for the other alkyl benzenes have been referred to this one.

where the hydrogen atom is abstracted from an atom bearing a C–O single bond it is difficult to be conclusive. Most of the rate constants included in Table 19 were used in order to obtain the numeric parameters in eqns. (24) and (25)¹⁴⁸; therefore, it is not surprising that these equations predict the right orders of magnitude. The main achievement of these equations is that IP_D correlates very well with the differences in reactivity.

It seems clear that for typical CT examples the RL model predicts a rate constant much lower than the experimental one, while the CT model agrees with experiment.

In the cases where the RL method is more successful (either predicting reactivities or selectivities) the CT method shows a clear trend to produce high estimates. If the observable reaction resulted from the kinetic competition between both mechanisms and eqns. (24) and (25) applied throughout one would expect the higher estimate to be the correct one. This is not the case for CT correlations.

Guttenplan and Cohen^{148,149} pointed out that the reactions involve "partial" charge transfer, rather than a full "one electron" transfer. The amount of charge transferred, as well as the energy associated with a given fraction of charge will

probably be determined by other molecular characteristics in addition to IP_D . Among these characteristics the type of orbital in which the electron involved is located ($n, \pi_{\text{aromatic}}, \pi_{\text{olefinic}}, \sigma$, etc.) can be expected to be particularly relevant. If this is the case, the correlations ($\log k$ vs. IP_D) should be labelled according to the type of electrons involved, rather than as "aliphatic" and "aromatic", which only takes into account the nature of the hydrocarbon groups. Equation (24) was derived from examples having n electrons or one olefinic double bond. Equation (25) was largely based on experimental data for molecules having aromatic groups, as well as n electrons. Benzene and toluene are the only two which do not fall in this group, although they correlate reasonably well with the others.

We note that the kinetic parameters for the interaction of butyrophenone triplets with methyl and ethyl amines (see Table 14 and ref. 153) cannot be correlated with IP_D . Presumably, for the smaller amines the changes in steric hindrance are also relevant.

Our conclusion is that with the present state of knowledge and understanding of the mechanism of these reactions it is not possible to give general rules as to which method or mechanism will apply best. However, it seems likely that both mechanisms are always in competition and some conclusions can be drawn for some particular cases:

(a) Molecules containing sulphur or nitrogen centres will frequently show typical CT behaviour (at least in solution). The data can be correlated using IP_D , while the RL model will lead to underestimates of the rate constant. The same argument probably holds for simple olefins.

(b) For simple aliphatic hydrocarbons the RL model will apply. The same seems to hold for tin compounds (nos. 16 and 17 in Table 19). Calculations for other ketones suggest that this is also true for silicon-hydrogen and halogen-hydrogen bonds.

(c) For aromatic hydrocarbons where the reaction results in the abstraction of a hydrogen atom from an aliphatic carbon-hydrogen bond the RL model seems to predict better the trends in reactivity, although both methods agree reasonably well with experiment.

(d) For molecules containing oxygen as the heteroatom both methods are only partly successful. In the examples involving ethers the experimental value falls between the two estimates. Quite probably the reaction involves a combination of both types of interaction, rather than a competition between the two mechanisms. Hopefully, studies of the temperature dependence of these reactions will throw light on this problem.

(e) Structural modification of the carbonyl compound will usually result in a change in the relative importance of both mechanisms. Typically, the presence of low lying π, π^* states and an increase in $-E(A^-/A)$ will favour the CT mechanism.

(f) When a CT mechanism is predominant, the limiting quantum yield will frequently be lower than the theoretical value.

(g) We note that the few examples involving amines which have been examined in the gas phase (Table 14 and ref. 153) seem to indicate that the abstractions in these cases should be regarded as *RL* mechanisms.

Miscellaneous

Yang *et al.*⁵⁸ have found a correlation between quantum yields of photo-reduction and radiative lifetimes. The results have already been included in Table 3.

S_{H2} reactions at the boron centre are frequently controlled by steric factors. In the case of the homolytic displacement by acetone triplets (see previous section) the rate constants can be correlated with steric factors which are available in the literature¹⁹⁸. This correlation is shown in Fig. 3.

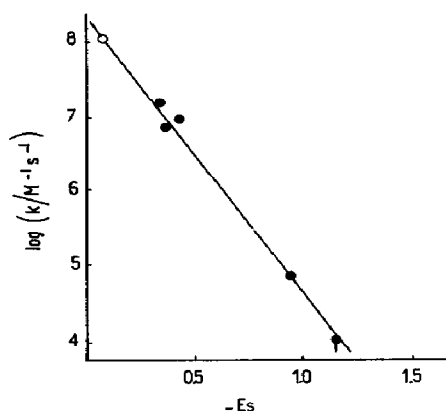


Fig. 3. Steric effects in the reaction of acetone triplets with various organoboranes. ●, in solution, ref. 4; O, in the gas phase, ref. 166.

FINAL COMMENTS

It has been frequently stated that "photoreduction" is one of the most extensively studied processes in photochemistry. This is probably true; however, there are a rather large number of questions which still remain wholly or partly unanswered, and we can only hope that future research will throw light on these points. The main questions are: (i) which is the temperature dependence of these reactions and to what extent is it phase dependent?; (ii) can the reactions of π, π^* states be explained by an equilibration model or are there true examples of reactions by π, π^* states?; (iii) are there examples of singlet state photoreductions?; (iv) which is the mechanism of the reaction of ketone triplets with amines *in the gas phase*?; and (v) what metallic centres apart from boron and tin are reactive in S_{H2} processes?

A recent report by Coyle¹⁹⁹ suggests that the Type II reaction of some aromatic esters can be regarded as genuine examples of intramolecular abstractions by π, π^ states.

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