

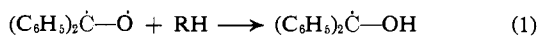
Hydrogen Abstraction Reactions by the Triplet States of Ketones¹

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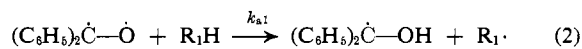
The products of photoreduction of benzophenone in the presence of a variety of substrates including aliphatic hydrocarbons are in accord with a simple scheme in which hydrogen abstraction by the benzophenone triplet is a rate-controlling step. A study of the competitive consumption of different hydrocarbons in the photoreduction reaction leads to a reactivity series very similar to that observed with *t*-butoxy radicals. The triplet shows a somewhat greater selectivity, and also a greater sensitivity toward electron availability, evidenced by a more negative Hammett ρ -value in the reactions of substituted toluenes. The energetics of triplet-hydrogen abstraction are shown to be very close to those for alkoxy radical reactions. Triplet states of acetophenone and several substituted benzophenones show very similar selectivities.

The ability of the triplet state of benzophenone and many other ketones to abstract hydrogen from suitable substrates is well known and recognized as a critical step in ketone photoreduction.²

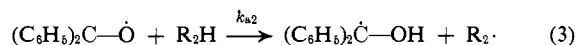


The rate of eq. 1 for several ketone-substrate combinations has been estimated by a number of workers³⁻⁵ by competitive quenching experiments and direct observation of triplet decay.

We have been interested in these hydrogen abstraction processes as a means for comparing the reactive properties of triplet states of ketones with those of simple alkoxy radicals which have been extensively investigated in this laboratory.⁶ It appeared that this might be done most expeditiously by simple competitive experiments involving the irradiation of benzophenone or other ketones in the presence of two (or more) substrates and determining their relative rates of disappearance.⁷ Under these conditions, the important reactions become, *e.g.*



and



whence

$$d \ln [\text{R}_1\text{H}]/d \ln [\text{R}_2\text{H}] = k_{a1}/k_{a2} \quad (4)$$

This approach renders unnecessary any determination of rate or quantum yield and bypasses any problems due to quenching of the triplet by other paths. It does, however, require the assumptions that RH groups cannot be regenerated from R· groups and that no chain processes are initiated leading to further consumption of substrate. The validity of these assumptions is considered further below.⁸

Results

Products. In the course of preliminary experiments it was found that the photoreduction of benzophenone occurs readily in a rather wider variety of substrates than was generally recognized, including simple aliphatic hydrocarbons.⁹ Since the products of photoreaction in cumene and toluene have already been examined by Hammond³ and shown to be simply those expected from the coupling of the radicals produced in eq. 1 (and accordingly indicate the validity of our analysis for these systems), they were not further investigated. The cyclohexane-benzophenone system was, however, studied in some detail. Photolysis in pure cyclohexane yielded only benzpinacol as a precipitate and bicyclohexyl, detected in the liquid phase by gas-liquid chromatography (g.l.c.). Since no cyclohexene was detected, we conclude that there is no significant regeneration of cyclohexane by disproportionation of cyclohexyl radicals. Photolysis of benzophenone in cyclohexane-benzene again yielded benzpinacol and approximately equal quantities of bicyclohexyl- and cyclohexylbenzene. The cyclohexylbenzene

(1) Taken from the Ph.D. Dissertation of M. J. Gibian, Columbia University, 1965. Support of this work by a grant from the National Science Foundation is gratefully acknowledged. For a preliminary report, cf. C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964).

(2) For general discussion and references, cf. G. S. Hammond and N. Turro, *Science*, **142**, 1541 (1963).

(3) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

(4) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

(5) J. A. Bell and H. Linshitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

(6) C. Walling, and B. B. Jacknow, *ibid.*, **82**, 6108 (1960), and subsequent papers.

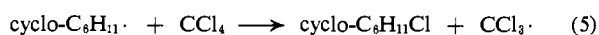
(7) A preliminary report of a similar investigation has recently been published by A. Padwa, *Tetrahedron Letters*, 3465 (1964); a comparison of his results with ours is given below.

(8) Recently we have results indicating that the determination of relative reactivities towards alkoxy radicals of molecules containing benzylic and aliphatic hydrogens via the analog of eq. 4 is subject to certain complications since benzylic hydrogen abstraction occurs by two paths: P. Wagner and C. Walling, to be published. Whether this difficulty also applies here is unknown, but we assume that relative reactivities determined by the same competitive method for the two species are probably still comparable.

(9) The photoreduction of acetone in cyclohexane was first described by N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958). Very recently the photoreduction of substituted benzophenones in cyclohexane has also been reported, G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964).

is an expected product of the addition of cyclohexyl radicals to benzene, and suggests an interesting technique for photochemical alkylation of aromatics. However, its formation requires addition followed by a subsequent dehydrogenation of an intermediate cyclohexylcyclohexadienyl radical. To the extent that cyclohexyl radicals are involved in the dehydrogenation step, cyclohexane will be regenerated, introducing a possible complication in competitive experiments in aromatic solvents.

Reaction in carbon tetrachloride was found to give almost quantitative yields (92–95% based on cyclohexane consumed) of cyclohexyl chloride,¹⁰ presumably *via* eq. 5. Since a roughly quantitative yield of



C_2Cl_6 was also obtained and *no* chloroform could be detected, further attack of $\text{CCl}_3\cdot$ radicals on cyclohexane must be negligible.

The essentially quantitative yield of cyclohexyl chloride obtained in the experiment just described suggested that the use of CCl_4 as a solvent would provide a convenient means of marking the point of triplet attack on molecules containing more than one type of C–H bond, and that relative yields of chlorides, as well as substrate disappearance, might be used to determine relative reaction rates in competitive experiments. Examples of this technique appear in the following sections.

Some other systems were examined more briefly. 2,3-Dimethylbutane in CCl_4 -chlorobenzene (added to increase benzophenone solubility) at both 20 and 100° gave chiefly 2-chloro-2,3-dimethylbutane with a trace of the 1-chloro isomer (g.l.c. peak areas 50–500 to 1) along with a higher boiling product, presumably dichloride. Similarly a neopentane-cyclohexane mixture in CCl_4 showed traces of neopentyl chloride, together with much more cyclohexyl chloride. Irradiation of benzophenone-2-propanol yielded acetone as expected (93 ± 6%) in three runs based on alcohol consumed. Similarly 2-octanol gave 2-octanone (69 ± 4%).

Competitive Reactions with Benzophenone. Competitive experiments were carried out by irradiating through a Nonex filter samples 0.02 to 0.4 *M* in two or more hydrocarbon substrates and 0.1–2.0 *M* in benzophenone, usually with benzene as solvent, in sealed, degassed tubes, and analyzing the products by g.l.c. against an inert internal standard. Results are summarized in Table I and are compared with data in the literature. Our values for compounds containing benzylic hydrogen are in quite good agreement with those reported by Padwa,⁷ but disagree with his data on cyclohexane and 2,3-dimethylbutane. We also find a larger difference between toluene and 2-propanol than that deduced from quenching measurements by Beckett and Porter.⁴

Although most experiments employed light filtered through Nonex, substitution of a Pyrex filter gave indistinguishable results. Also substitution of chlorobenzene or acetic acid for benzene as solvent had no effect on relative reactivities in toluene-cyclohexane

(10) Cyclohexyl chloride is also formed in Freon 112 ($\text{CFCl}_2\text{CFCl}_2$). In fact, its formation was first noted in an attempt to use this Freon as an inert internal standard for g.l.c. analysis.

Table I. Relative Reactivities of Substrates toward Hydrogen Abstraction by the Triplet State of Benzophenone (22 ± 3°)

Substrate	Relative reactivities ^a	Lit.	$k_a \times 10^{-3b}$
<i>p</i> -Methoxytoluene	10.6 ± 0.1 (2)		95
2-Octanol	10.2 ± 0.6 (3)		92
2-Propanol	9.7 ± 0.5 (3)	1.2 ^c	87
Mesitylene	5.6 ± 0.3 (6)	5.34 ^d	50
<i>p</i> -Xylene	4.3 ± 0.2 (3)		39
Cumene	3.3 ± 0.2 (12)	2.88, ^d 3.5 ^e	30
Cumene ^f	2.4 ± 0.4 (6)		...
<i>m</i> -Xylene	2.9 ± 0.1 (6)		26
Cyclohexane	2.2 ± 0.2 (13)	4.08 ^d	20
Cyclohexane ^f	2.8 ± 0.3 (6)		...
2,3-Dimethylbutane	2.0 ± 0.1 (3)	0.84 ^d	18
<i>p</i> -Fluorotoluene	1.2 ± 0.1 (6)		11
Toluene	1.00 (standard)	1.00	9.0
<i>p</i> -Chlorotoluene	0.97 ± 0.02 (3)		8.7
Anisole	0.53 ± 0.05 (5)		4.8

^a Experimental error is average deviation of number of determinations shown in parentheses. ^b Rate constant for reaction 1 (see Discussion). ^c See ref. 4. ^d See ref. 7. ^e See ref. 3. ^f At 100°.

and toluene-cumene systems. Acetic acid and carbon tetrachloride, incidentally, proved to be quite inert to the triplet state of benzophenone. The ketone was recovered unchanged after prolonged irradiation in these media alone.

Other Carbonyl Compounds. Reactivities of cyclohexane and cumene relative to toluene were investigated employing several other ketones with results listed in Table II. Values for the effective substituted

Table II. Comparison of Selectivity of Triplet States of Ketones (Toluene = 1.0)

Ketone	Cyclohexane ^a	Cumene ^a
Benzophenone (B)	2.2 ± 0.2 (13)	3.3 ± 0.2 (12)
4,4'-Dimethyl B	2.2 ± 0.2 (6)	3.7 ± 0.3 (6)
4-Methoxy B	2.6 ± 0.5 (7)	3.3 ± 0.4 (7)
4-Chloro B	...	3.0 ± 0.3 (13)
Acetophenone	3.0 ± 0.8 (8)	2.3 ± 0.7 (8)
4-Nitro B	^b	
4,4'-Dimethylamino B	^b	
2-Acetonaphthone	^b	
Fluorenone	^b	

^a Experimental error is average deviation of number of experiments indicated in parentheses. ^b No hydrocarbon reacted.

benzophenones are experimentally indistinguishable from benzophenone. Acetophenone triplet results suggest a slightly increased reactivity for cyclohexane and decreased reactivity for cumene. The effect, while small, parallels the trend of Padwa's data⁷ for the same systems. The negative results for the last four ketones in Table II are not unexpected. 2-Acetonaphthone and 4,4-dimethylaminobenzophenone are known to give $\pi \rightarrow \pi^*$ triplets on photoexcitation.¹¹ Fluorenone yields a $n \rightarrow \pi^*$ triplet of relatively low energy (53

(11) Porter and Suppan⁹ have noted that *p*-aminobenzophenone, which is inert in 2-propanol, is photoreduced in cyclohexane and conclude that, in this solvent, the $n \rightarrow \pi^*$ triplet represents the lowest excited state. Evidently the same crossover does not occur here.

kcal.)¹² and short life, and aromatic nitro compounds frequently interfere with radical processes.

Discussion

As we have seen, the products of the photoreduction of benzophenone and similar ketones are consistent with a simple scheme of rate-determining steps for substrate consumption which should make competitive experiments a valid measure of relative reactivity.¹³ In fact, our cyclohexane experiments suggest a rather simple way of generating alkyl radicals in a variety of media.

Our primary objective in this study was to compare the relative reactivities of substrates towards the triplet states of ketones with those towards simple alkoxy radicals, and in Table III this is done for benzophenone

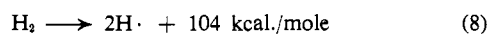
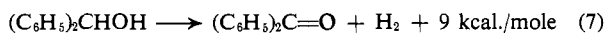
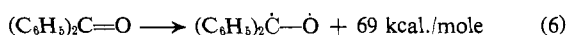
Table III. Relative Reactivities of Substrates toward Benzophenone Triplet and *t*-Butoxy Radicals (per Hydrogen)

Substrate	Triplet (22°)	C ₄ H ₉ O· (40°) ^a
2,3-Dimethylbutane (1°)	<0.01 ^b	0.1
(3°)	3.0	4.2
Cyclohexane (2°)	0.5	1.5
Toluene (std.)	1.0	1.0
Ethylbenzene	4.6 ^c	3.2 ^d
Cumene	9.9	6.8 ^d

^a See ref. 6. ^b On the basis of a ratio of 3°/1° chloride of at least 50 for reaction in CCl₄. ^c See ref. 7. ^d α-Hydrogens.

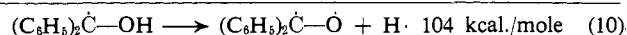
triplet and the *t*-butoxy radical, generated from *t*-butyl hypochlorite. Qualitatively, the two reactions are very similar, although the benzophenone triplet is somewhat more selective, particularly between aliphatic compounds with relatively strong C–H bonds. This sensitivity to bond strength would also account for the reversal of cyclohexane–toluene reactivities. Presumably reactivities parallel activation energies in this sort of series, and we may note (Table I) that cumene–toluene selectivity decreases with increasing temperature. On the other hand, cyclohexane–toluene increases, implying that the cyclohexane reaction has the higher activation energy and higher *PZ* factor. This is plausible and is qualitatively corrected for in Table III where reactivities are corrected to a per C–H basis.

The similarity of ketone triplets and alkoxy radicals which we find here in their reactions is plausible on both thermochemical and electronic grounds. The energetics of hydrogen abstraction by benzophenone triplet requires knowledge of $D((C_6H_5)_2\dot{C}O-H)$ which may be obtained from the following thermochemical cycle.



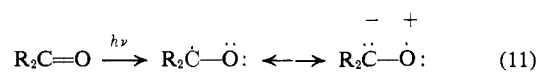
(12) W. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(13) A complication which we have not mentioned is the possible reversibility of eq. 2 and 3. However, this has specifically been shown *not* to occur with 2-butanol since recovered optically active alcohol has not undergone racemization: J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Marton, *ibid.*, **81**, 1068 (1959).



Here eq. 6 is the triplet excitation energy of benzophenone known from spectroscopic data,¹² and eq. 7 and 8 are available from standard thermochemical tables. The energetics of eq. 9 is estimated on the basis that it should lie between $D((C_6H_5)_3C-H)$ and $D(C_6H_5-CH_2-H)$. The first quantity is close to 75 kcal. from ΔH values of hydrogenation and dissociation of hexaphenylethane.¹⁴ Considering its importance, $D(C_6H_5-CH_2-H)$ is still distressingly uncertain. Several results obtained prior to 1960 favor approximately 77 kcal.,¹⁵ but recent determinations have been as high as 85 kcal.¹⁶ Accordingly, although our guess of 78 kcal. gives the same value for $D((C_6H_5)_2CO-H)$, as the usually accepted value for $D(t-C_4H_9O-H)$, 104 kcal.,¹⁷ it is uncertain by at least 3 kcal.

Electronically, $n \rightarrow \pi^*$ excitation involves promotion of an electron in one of the unshared pairs of oxygen to the antibonding state of the carbon–oxygen π -bond, a situation which may be symbolized in valence bond terms¹⁸ as eq. 11. The left-hand resonance structure



represents the major contribution, so the triplet approximates a species with seven electrons on single-bonded oxygen. On the other hand, contributions from the right-hand structure contribute a positive charge to oxygen and could make it a more strongly electron-accepting species.

Effects of polar substituents on toluene reactivity are listed in Table IV, compared with data for the *t*-butoxy radical.

Table IV. Relative Reactivities per Hydrogen of Substituted Toluenes

Substituents	(C ₆ H ₅) ₂ C–O	C ₄ H ₉ O· (40°) ^a	C ₄ H ₉ O· (0°) ^b
4-Methoxy	10.1 ^c		
4-Methyl	2.15	1.53	1.43
3,5-Dimethyl	1.9	1.33	...
3-Methyl	1.45	1.17	1.16
4-Fluoro	1.2	...	0.94
4-Chloro	0.97	0.71	0.70
3-Chloro	...	0.52	0.49

^a C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6113 (1960). ^b In acetonitrile solvent, unpublished experiments by Dr. P. Wagner in these laboratories. ^c Corrected for attack on –OCH₃, assumed to be the same as that on anisole.

Hammett ρ - σ plots of the data using both σ and σ^+ are shown in Figure 1, and it is evident that σ^+ -parameters give a better fit, corresponding to $\rho = -1.16$ with a correlation coefficient of 0.981. For the *t*-butoxy radical at 40°, $\rho = -0.83$ for reactivities

(14) Cf. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 530

(15) Reference 14, Chapter 2.

(16) Cf. for example, G. L. Esteban, J. A. Karr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3873 (1963).

(17) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(18) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

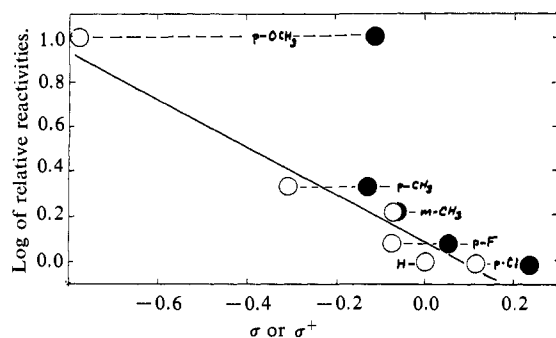


Figure 1. Relative reactivities of substituted toluenes towards benzophenone triplet: solid circles, vs. σ ; open circles, vs. σ^+ .

plotted against σ ,¹⁹ and Wagner's data at 0° gives $\rho = -0.96$. Whether σ^+ -constants would give a better fit would require data for 4-methoxy and other substituents with large σ - σ^+ differences, but, if so, would give a line of certainly lower slope. Thus we find that the benzophenone triplet indeed shows a greater sensitivity to substrate polarity, but whether this is due to its being a more "electronegative" radical or to the hydrogen abstraction being simply a more selective higher activation energy process²⁰ is open to question. In any case, however, its inertness towards acetic acid and high reactivity toward secondary alcohols (per hydrogen, 2-propanol is 53 times as reactive as cyclohexane) indicates that the triplet shows a great sensitivity to electron availability. If polarity is important, ρ -values might be expected to vary with triplet structure. However, our experiments listed in Table II indicate that any such effect must be very small.

Finally, combination of our results with literature data permit calculation of actual rate constants for hydrogen abstraction by the benzophenone triplet, and these are listed in the last column of Table I. Hammond³ has determined the relative rates for reaction of the triplet with toluene and the quenching agent ferric dipivaloylmethide and gives k_r/k_q (k_a/k_q in our terminology) as 10^{-5} . The best value of k_q appears to be the one measured directly in flash photolysis experiments by Bell and Linshitz,⁵ $k_q = 0.9 \times 10^9$. Combining these gives k_a (toluene) = 9×10^3 , and our relative reactivities provide the other values listed. We see that all rates lie in the range 10^3 - 10^5 . Since the *t*-butoxy radical shows a lower selectivity than the triplet, one might infer that its reactions are even faster.

Experimental

Photolyses were carried out in sealed, degassed tubes arranged circumferentially around a Hanovia 450-w., medium-pressure, mercury-vapor, quartz immersion lamp in a Vycor well with Nonex filter sleeve all contained in a water bath held at $22 \pm 3^\circ$. In a few runs

(19) See Table IV, footnote *a*.

(20) Thus $\text{Br}\cdot$ shows a much more negative ρ -value than $\text{Cl}\cdot$, although it is an atom of lower electronegativity. For a tabulation of ρ -values, see G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

(and those employing acetophenone) a Pyrex glass sleeve was substituted for the Nonex. Some preparative experiments were carried out under nitrogen in a 80-cc. photolytic apparatus of conventional design with a lamp in a central well. In runs at 100° , samples were irradiated in a boiling water bath.

Product Studies. Photoreduction of benzophenone (0.58 g.) in 5 ml. of cyclohexane was complete in almost 2 weeks. Benzpinacol was the only solid product, and only bicyclohexyl could be detected by g.l.c. Benzhydrol and cyclohexene were both absent. Photoreduction of 10.8 g. of benzophenone in 27.6 g. of cyclohexane and 100 ml. of benzene gave a copious precipitate of benzpinacol after 5 days, and g.l.c. analysis showed equal yields of bicyclohexyl and cyclohexylbenzene, identified by collection and comparison with known material. Chromatography on silica gel yielded a single product, which from infrared spectra was a mixture of benzpinacol and benzpinacone, presumably formed by rearrangement during chromatography. Photoreduction experiments carried out in CCl_4 yielded cyclohexyl chloride (92 and 95% based on cyclohexane consumed), and C_2Cl_6 (roughly quantitative yield, although peak areas were not calibrated). Chloroform and cyclohexene were shown to be absent. Photoreduction products of benzophenone in 2,3-dimethylbutane were yellow in color, and some HCl was evolved in the reaction. However, g.l.c. indicated only three volatile products, 1-chloro-2,3-dimethylbutane, 2-chloro-2,3-dimethylbutane (peak areas 50-500:1), and a less volatile product (approximately 4% of total) presumed to be dichloride.

Competitive experiments were carried out essentially as in our *t*-butyl hypochlorite work.⁶ A number of tubes were irradiated at one time. Since photoreduction rates varied considerably between systems, tubes were removed periodically and analyzed by g.l.c. until optimum conversion times for analysis had been determined. In a typical experiment, 36 mmoles of benzophenone, 6.7 mmoles of toluene, 6.5 mmoles of *p*-fluorotoluene, 7.8 mmoles of *m*-xylene, 8.3 mmoles of anisole, and 8.6 mmoles of *o*-dichlorobenzene (as internal standard) were mixed with 15 ml. of benzene, and 5 ml. of the mixture was placed in each of four tubes which were sealed and degassed. One tube was used to determine initial peak areas in the g.l.c. analysis, and the others were irradiated for 40, 49, and 80 hr., respectively. At the end of this time roughly 40% of the substrates had been consumed, and results appear in Table V.

Table V. Competitive Reaction of Toluene, *p*-Fluorotoluene, *m*-Xylene, and Anisole with Benzophenone Triplet

	[RH]/[RH] ₀			Relative reactivities ^a
	40 hr.	49 hr.	80 hr.	
Toluene	0.854	0.845	0.762	1.00
<i>p</i> -Fluorotoluene	0.846	0.817	0.708	1.18 ± 0.08
<i>m</i> -Xylene	0.627	0.575	0.443	3.08 ± 0.15
Anisole	0.952	0.910	0.869	0.47 ± 0.10

^a Relative to toluene, experimental error is the average deviation.