J. Am. Chem. Soc. **1996,** *118,* 746−754

Photoinduced Radical Cleavage of Bromophenyl Ketones

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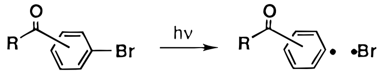
Received August 14, 1995[⊗]

Abstract: Several bromophenyl alkyl ketones undergo photoinduced radical cleavage of bromine atoms; the resulting acylphenyl radicals are trapped as the dehalogenated ketones either by alkane solvents or by added thiols. Quantum yields for this process decrease with increasing solvent viscosity; this behavior indicates that recoupling of the phenyl/bromine radical pairs competes with their diffusion apart. In some cases Norrish type II elimination competes with the cleavage reaction. Steady state studies indicate room temperature rate constants for triplet state C−Br radical cleavage of 2 and 1×10^8 s^{-1}, respectively, for *m*- and *p*-bromoacetophenone. Flash kinetics measurements of the temperature dependence for their triplet decay provided activation parameters for triplet state cleavage: $\Delta S^{\ddagger} = -5$ eu for the para isomer and −3 eu for the meta; $\Delta H^{\ddagger} = 5.3$ kcal/mol for both. The values for the meta isomer are the same in methanol and toluene and extrapolate to the room temperature decay rate measured by steady state techniques. The 0.002−0.003 quantum yields for conversion of *m*- and *p*-bromobenzophenone to benzophenone in cyclopentane solvent indicate triplet state cleavage rates of $0.8-1.0 \times 10^5$ s^{-1}, which would suggest $\Delta H^{\ddagger}$ values near 10 kcal/mol. Consideration of triplet excitation energies and of the phenyl−Br bond strength suggests a mechanism for triplet cleavage involving activated C−Br bond stretching in the triplets until a π,π^* configuration is converted into a dissociative n^{π}_{Br},σ^* state. It is suggested that the different isomers have comparable mixing of n^{π}_{Br},π^* character into their π,π^* triplets and that the state interconversions occur inefficiently at surface crossings with a n^{π}_{Br},σ^* state. The *o*-bromo ketones show unusual behavior. The Arrhenius plot for triplet decay of *o*-bromoacetophenone is curved and only half the total cleavage can be quenched by naphthalene. *o*-Bromobenzophenone is 500 times more reactive than its isomers; direct interaction between bromine and carbonyl as well as steric depression of the C−Br dissociation energy may both contribute to this unusual reactivity.

Introduction

The photoinduced cleavage of carbon−halogen bonds in aryl halides is well-known.[1,2] Direct irradiation of iodo-, bromo-, and chlorobenzene produces phenyl and halogen radicals. Defining the exact nature of the excited states responsible for this cleavage has remained a challenging goal, mixing of π,π^* states with π,σ^* or σ,π^* states[4] and internal conversion to a dissociative σ,σ^* or π,σ^* state[5−7] being common suggestions. Bersohn first examined the photodissociation of several bromo and iodo aromatics by molecular beam studies and found that the former cleave much slower than the latter, with both presumably involving triplet states.[5]

Although a variety of substituted halobenzenes undergo photoinduced cleavage, very little is known about how substituents other than the halogen affect excited state reactivity. In this regard we thought it worthwhile to study halophenyl ketones, since the well-known rapid intersystem crossing of phenyl ketones[8] should confine reactivity to triplet states. Moreover, excitation is confined to relatively well-defined n,π^* and π,π^* triplets, with excitation energies that can be varied with extra substituents. Very little prior work had been reported on the photoinduced radical cleavage of halophenyl ketones. Fluoro- and chlorobenzophenones undergo only normal photoreduction to halopinacols.[9,10] This result was to be expected given that the C−X bond energies of such ketones are much higher than their ∼68 kcal/mol triplet energies. Baum and Pitts reported that some bromo- and iodophenyl ketones are photoreduced to the dehalogenated phenyl ketones.[10] Their studies indicate that radical cleavage reactions do occur but unfortunately provided no direct measures of actual rate constants for cleavage. Therefore we have investigated the triplet state reactivity of various halophenyl ketones with the intent of establishing how triplet configuration and energy affect rate constants for cleavage of C−X bonds. This paper reports results for bromophenyl ketones. We recently have reported the behavior of iodobenzophenones[11] and communicated the different behavior of iodo and bromo ketones.[12]



Results

Competing Photoreactions of Bromo Ketones. The four ketones *p*-bromovalerophenone (**pBrV**), *m*-bromovalerophenone

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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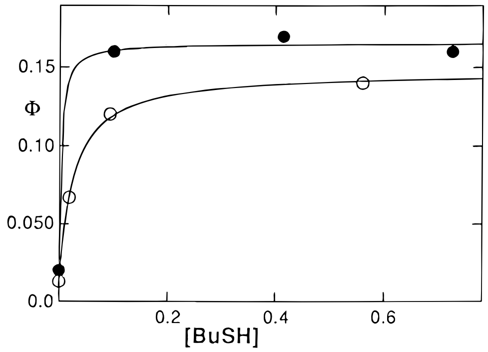

Figure 1. Effect of added butanethiol on quantum yields for dehalogenated phenyl alkyl ketone from (○) **pBrV** and (●) **pBrB** in benzene.

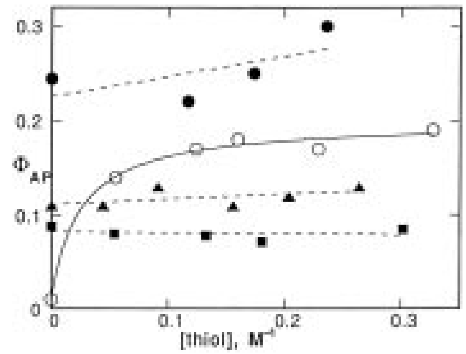

Figure 2. Effect of added thiol in solvents of different viscosity on quantum yields for formation of acetophenone from (●) **pBrA** in *n*-hexane, (○) **pBrA** in benzene, (▲) **mBrA** in cyclohexane, and (■) **oBrA** in cyclooctane.

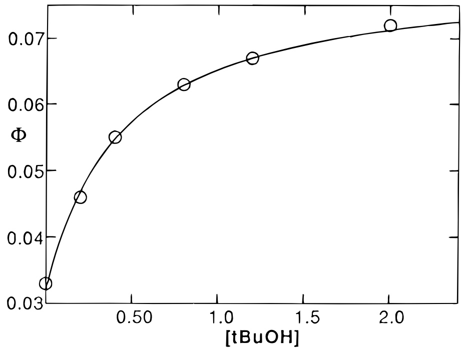

Figure 3. Effect of added alcohol on quantum yield for *p*-bromoacetophenone formation from **pBrV**.

Table 1. Photokinetics for Competitive Halogen Cleavage and Norrish Type II Elimination or Photoreduction[a]

ketone	$\Phi_{-\mathrm{rctnt}}$	Φ_{II}	$\Phi_{\mathrm{II}}^{\max}$ [b]	Φ_{cl}	$\Phi_{\mathrm{cl}}^{\max}$	Φ_{B}	$k_q\tau$, M^{-1}
mBrV	0.17	0.087	0.25	0.007	0.07[c]	0.038	17 ± 2
pBrV	0.10	0.033	0.072	0.014	0.14[c]	0.021	34 ± 3[d]
pBrB	0.12	<0.001	<0.002	0.02	0.17[c]	0.034	58 ± 6
pClB		0.43		<0.001	0.005[c]	0.0013	2000[e]
oBrA[f]				0.16	0.38[g]		24
pBrBzP[f]				0.002	0.003[h]		
mBrBzP[f]				0.0013	0.002[h]		
oBrBzP[f]				0.09	0.38[g,h]		110

[a] In benzene unless otherwise noted. [b] 2 M *tert*-butyl alcohol. [c] 0.5 M butanethiol. [d] 31 for quenching of *p*-bromoacetophenone formation; 36 for quenching of valerophenone formation. [e] Calculated from data for butyrophenone and *p*-chlorovalerophenone, ref 21. [f] In cyclopentane. [g] In benzene. [h] 0.03 M *n*-$C_8H_{17}SH$ added.

(**mBrV**), *p*-bromobutyrophenone (**pBrB**), and *p*-chlorobutyrophenone (**pClB**) were synthesized as described in the Experimental Section. Irradiation of degassed benzene solutions of each halo ketone gave mixtures of products from Norrish type II hydrogen abstraction and from radical C−X bond cleavage: the haloacetophenones and minor amounts of what are assumed to be cyclobutanols; the corresponding dehalogenated phenyl ketones; and a fourth product **B**, shown to be *p*-phenylvalerophenone in the case of **pBrV**. As already reported,[10b] **pBrB** undergoes primarily radical cleavage and produces negligible type II product. When the reactions were run in the presence of added butanethiol, no biphenylyl ketone **B** was formed and the yields of dehalogenated phenyl ketone were enhanced. Likewise the addition of *tert*-butyl alcohol enhanced yields of the Norrish type II products, except for **pBrB** which forms no measurable type II product.

The three isomeric bromoacetophenones **o-**, **m-**, and **pBrA** were irradiated in benzene with added thiol and in several alkane solvents with and without added thiol. In all cases acetophenone was the predominant organic product, representing >96% of the **BrA** reacted. The fate of the other radical species was not scrutinized quantitatively; but combined GC-mass spectrometric analysis showed that cyclohexyl bromide (30%) and bicyclohexyl were formed when **pBrA** was irradiated in cyclohexane solvent. HBr was also detected. Bromine atoms, unlike iodine atoms,[11] apparently abstract hydrogen atoms from solvent[13] in competition with their dimerization. When the **BrA**'s were irradiated in benzene alone, the solutions took on the reddish tinge of Br_2. The three bromobenzophenones **o-**, **m-**, and **pBrBzP** were irradiated in benzene with added octanethiol and in cyclopentane with and without added thiol. In all cases benzophenone was formed, as already reported for the ortho and para isomers,[10a] together with the expected photoreduction products[9] from the meta and para isomers. The ortho isomer, however, undergoes primarily dehalogenation, forming benzophenone in 92% yield in cyclohexane, together with bromocyclohexane and a small amount of fluorenone.

Quantum yields for the various products were determined by parallel irradiation (313 nm) of degassed, sealed tubes containing solutions 0.02−0.05 M in halo ketone. Actinometer solutions containing 0.1 M valerophenone in benzene[14] were irradiated at the same time. Product yields were then determined by GC or HPLC analysis. Figure 1 shows the effect of added thiol on the quantum yields for reduction of two of the ketones in benzene, the high concentration limit representing complete scavenging of photoproduced aryl radicals.[15] Figure 2 shows the effect of added thiol on quantum yields for acetophenone formation from bromoacetophenones in various alkane solvents. Figure 3 shows the usual effect of added alcohol[15,16] on acetophenone yields from **pBrV**.

Table 1 lists the quantum yields for product formation and reactant disappearance for all the halo ketones under different conditions. It also lists $k_q\tau$ values described by the slopes of linear Stern−Volmer quenching plots. These were obtained by measuring product yields from 365-nm excitation in the presence of various concentrations of naphthalene. Decreases in both dehalogenation and type II elimination were measured, with good agreement between $k_q\tau$ values measured both ways for **pBrV** when butanethiol was included to trap all of the acylphenyl radicals. Only half of the dehalogenation of **oBrA** is quenched by naphthalene; the value of $\Phi°/\Phi$ plateaus at 2 at

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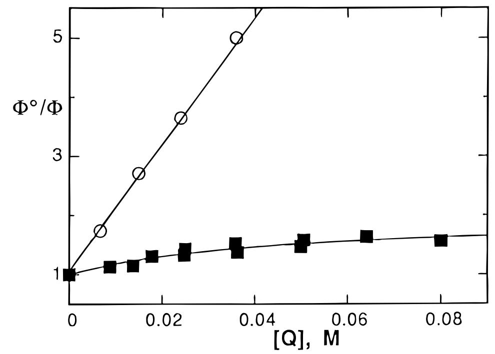

Figure 4. Quenching by naphthalene of benzophenone formation from **oBrBzP** (○) and acetophenone formation from **oBrA** (■), both in cyclohexane.

Table 2. Maximized Quantum Yields for Reductive Dehalogenation of Bromophenyl Ketones in Various Solvents

solvent	viscosity, cP (at 25 °C)	**oBrA**	**mBrA**	**pBrA**	**oBrBzP**
hexane	0.29	0.25	0.23	0.24	0.12
benzene	0.63	0.16	0.03	0.01	0.09
benzene[a]	0.63	0.38	0.28	0.17	0.38
cyclohexane	0.88	0.15	0.11	0.12	0.07
cyclooctane	2.16	0.08	0.07	0.04	0.03

[a] With 0.1 M dodecanethiol or octanethiol.

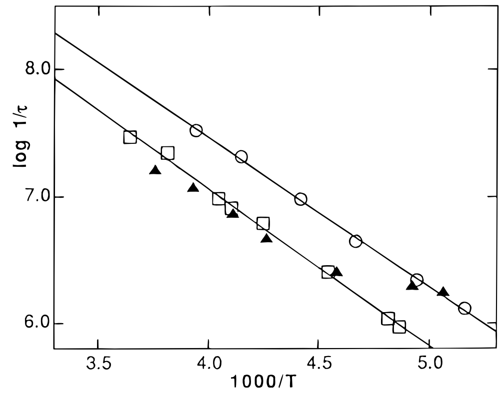

Figure 5. Arrhenius plots of triplet decay for (□) **pBrA** and (▲) **oBrA** in toluene and (○) **mBrA** in methanol.

high concentrations of 1-methylnaphthalene. Figure 4 compares the curved Stern−Volmer plot for **oBrA** to the linear plot for **oBrBzP**. The $k_q\tau$ value for **oBrA** was derived by nonlinear least-squares analysis of the data.[17] No such curvature was evident in quenching plots of *m*- and *p*-bromo ketones.

Table 2 lists maximum quantum yields for formation of acetophenone from the bromoacetophenones in different alkane solvents. As shown in Figure 2 added thiol generally has only small effects on these values, although it appears to generally raise quantum yields somewhat in hexane but not in the more viscous solvents.

Flash Kinetics. Laser flash excitation of toluene solutions ~0.005 M in *o*-, *m*-, or *p*-bromoacetophenone produced strong T−T absorption between 400 and 450 nm together with an absorption maximum at ~550 nm characteristic of the bromine atom−benzene complex.[18] Decay lifetimes of the triplet signals were measured between 190 and 290 K in methanol. The resulting Arrhenius plots are shown in Figure 5. Those for the meta and para isomers are linear (an identical plot was obtained for the meta isomer in toluene), whereas that for the ortho isomer plateaus at low temperatures. The plots are extrapolated to room temperature for comparison of decay rates with those determined by quenching studies.

Table 3. Spectroscopic Features of Halophenyl Ketones

ketone	L_a λ_{max} (ϵ)[a]	n,π^* λ_{max} (ϵ)[a]	phosp 0,0 (kcal/mol)[b]
pBrV	252 nm (19 000)	325 nm (68)	399 nm (71.7)[c]
pBrA			405 nm (70.6)[d,h]
pClB[e]	249 nm (18 500)	325 nm	406 nm (70.5)[c] 396 nm (72.3)[d]
mBrV	239 nm (7 200)	326 nm (47)	396 nm (72.2)[d]
mBrA			396 nm (72.2)[h]
mClB	239 nm (10 000)	326 nm	405 nm (70.6)[f] 389 nm (73.6)[d]
oBrA	237 nm (8 000)	316 nm (sh) (~80)	400 nm (71.5)[h]
pBrBzP			(68.9)[c,g]
mBrBzP			(68.3)[c,g]
oBrBzP			412 nm (69.5)[h]

[a] In heptane. [b] At 77 K. [c] In 4:1 methylcyclohexane/isopentane. [d] In 4:1 methanol/ethanol. [e] From ref 21. [f] In isopentane. [g] From ref 19. [h] In 2-methyltetrahydrofuran.

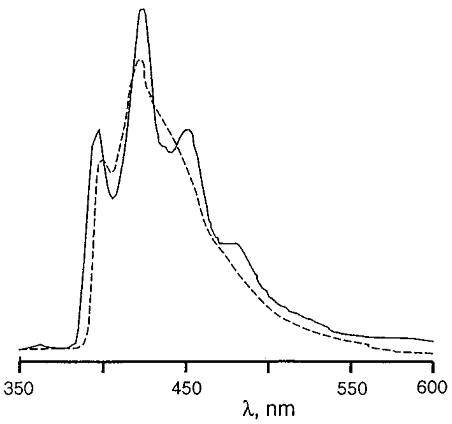

Figure 6. Phosphorescence at 77 K in methyltetrahydrofuran glasses of (—) **mBrA** and (- - -) **pBrA**.

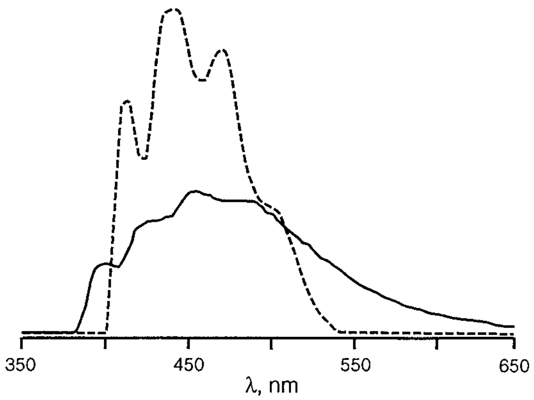

Figure 7. Phosphorescence at 77 K in methyltetrahydrofuran glasses of (—) **oBrA** and (- - -) **oBrBzP**.

Spectroscopy. Table 3 lists the major spectroscopic features of these bromophenyl ketones. Two chloro ketones are included for the sake of comparison; it appears that bromo and chloro substitution have nearly identical effects on both UV and phosphorescence spectra. Figure 6 compares the phosphorescence spectra of the *m*- and *p*-bromoacetophenones and Figure 7 those of the *o*-bromo ketones.

Discussion

Two facts indicate that the photochemical reactions of all these bromophenyl ketones (with the exception of **oBrA**) arise from their triplet states: (1) both cleavage and γ-hydrogen

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abstraction are quenchable by normal triplet quenchers; and (2) the decay kinetics of the transients observed by flash spectroscopy reveal the same cleavage rate constants as those gleaned from the steady state quenching studies.

Nature of Triplets. That halobenzophenones have n,π^* lowest triplets is well established.[19] Even **oBrBzP** displays phosphorescence with sharp features and typical n,π^* vibronic structure. Such is not the case for many substituted phenyl alkyl ketones.[20,21] The major broadening of the phosphorescence spectra of the *p*-bromo phenones suggests that their lowest triplets are π,π^* in nature, as is the case for *p*-chloroacetophenone.[22] Their UV absorption reveals CT stabilization of the ^1L_a state and thus of the triplet. This effect is slightly larger than for the *p*-chloro ketones. There is no difference between the absorption of the *m*-chloro- and *m*-bromophenones and they all display nicely structured phosphorescence spectra; but the bromo ketones emit at lower energy. It is likely that a meta bromine can stabilize the π,π^* triplet by charge transfer such as happens with a methoxy substituent,[21] but emission still occurs from a nearby n,π^* triplet.[22] The **oBrA** emission spectrum is broadened but still shows n,π^* vibronic structure. Together the spectra suggest that n,π^* and π,π^* triplets of the bromophenones have similar energies for all three substitution patterns.

Reactions of Triplets. In some cases radical C−Br bond cleavage competes with hydrogen abstraction either from a γ-carbon or from solvent; in others it is the sole reaction. Thus the quantum yields for Norrish type II elimination from the bromo ketones are lower than those of the corresponding chloro ketones[21] and are accompanied by typical radical trapping products, especially the dehalogenated phenyl ketone. The bromine atoms were not specifically trapped but were detected by flash spectroscopy as the benzene complex. The very low quantum yields for benzophenone formation from **mBrBzP** and **pBrBzP** reveal that cleavage is much slower than the known rapid hydrogen abstraction from cyclopentane.[9] In contrast, **oBrBzP** undergoes cleavage very efficiently, as do the bromoacetophenones.

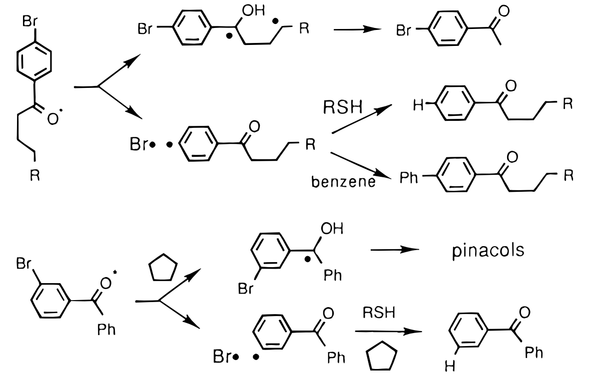

Table 4. Rate Constants (10^8 s^{-1}) for Triplet Halo Ketones[a]

ketone	$1/\tau$[b]	model k_H[c]	k_H	k_{-X}
mBrV[d]	3.5	1.8	1.0	2.5
pBrV[d]	1.75	0.4	0.4	1.35
pBrB[d]	1.0	0.02[e]	0.02	1.0
pClB[d]	0.02	0.02[e]	0.02	0.00015
oBrA[f]	3.0[g]			3.0
mBrA	2.5 (2 0)[h]			2.0
pBrA	1.0 (0.7)[h]			0.7
oBrBzP[f]	0.6[g]	<0.001		0.6
mBrBzP[i]	0.076[j]	0.076	0.076	0.0008
pBrBzP[i]	0.063[j]	0.063	0.063	0.0010

[a] At room temperature. [b] Derived from $k_q\tau$ values, with $k_q = 6 \times 10^9$ M^{-1} s^{-1}. [c] Analogous chloroketone, ref 21. [d] In benzene. [e] Extrapolated from the value for butyrophenone by the effect of *p*-Cl on valerophenone. [f] In cyclohexane. [g] Based on $k_q = 7 \times 10^9$ M^{-1} s^{-1}, ref 23b. [h] Value extrapolated from Arrhenius plots in toluene and/or methanol. [i] In cyclopentane. [j] Value for the corresponding chlorobenzophenone, ref 9.

Table 4 dissects the triplet lifetimes gleaned from the $k_q\tau$ values and quantum yields into competing rate constants for hydrogen abstraction and radical cleavage. A value of 6×10^9 M^{-1} s^{-1} was used for k_q.[23] We assume that k_H values for the bromo ketones should be similar to those for the corresponding chloro ketones already studied, with para substitution slowing hydrogen abstraction by stabilizing the unreactive π,π^* triplet and meta substitution producing a small inductive rate enhancement for the n,π^* triplet.[9,21] The tiny type II quantum yield for **pBrB**, noted by Baum et al.,[10b] is consistent with the low k_H value for **pClB** and sets k_{-Br} at 1×10^8 s^{-1}. The faster triplet decay of **pBrV** is consistent with a similar value for k_{-Br} and a k_H value the same as that for *p*-chlorovalerophenone. The measured type II quantum yield for **mBrV** is 28% that for *m*-chlorovalerophenone and indicates the k_H and k_{-Br} values listed. The k_H value is only half that for the model chloro ketone and suggests some lowering of the π,π^* triplet by electron donation from the bromine, as suggested above.

It is noteworthy that a meta bromine cleaves faster than a para bromine, a fact disguised by the relative product quantum yields from **mBrV** and **pBrV.** (The type II yield from the latter is low enough that it was missed in an earlier study.[21]) The deceptively high meta/para type II ratio is caused by the large depression of the hydrogen abstraction rate caused by a para bromine.[21]

The very low cleavage rate constant for **pClB** was estimated by multiplying the extrapolated triplet lifetime by estimated quantum efficiencies for cleavage. The values for the bromobenzophenones required similar calculation. The triplet decay rate for **pBrBzP** has been measured in alkane solvent[24] and closely matches the decay rate of *p*-chlorobenzophenone in cyclopentane, which represents hydrogen abstraction from solvent.[9] Thus the triplet lifetimes of both isomers were assumed to equal those of the chloro ketones.[9] These lifetimes were first multiplied by the maximum cleavage quantum yields and then, in order to correct for revertible cleavage (see below), divided by 0.18, the quantum yields of acetophenone formation from the corresponding bromoacetophenones in cyclopentane. The cleavage rates of the bromoacetophenones estimated from quenching of the bromovalerophenones match those measured by direct flash kinetics well.

Radiationless Decay to Hot Ground States? A referee has suggested that the bromine atoms might induce sufficent spin−orbit coupling in the triplets to promote radiationless decay to vibrationally excited ground state reactant, which could then undergo bond cleavage by rapid redistribution of vibrational energy into the relatively weak C−Br bond. This generic possibility has been discussed over the years for most photochemical cleavage reactions and rarely found to be important in solution because of the rapid transfer of vibrational energy

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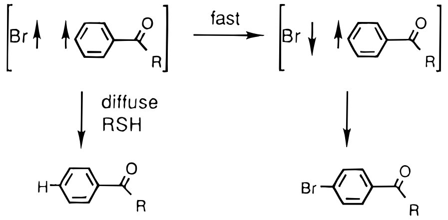
to solvent. Thus we doubt that such radiationless decay is responsible for efficient C−Br bond cleavage; but it could explain quantum yields <50% for radical formation. Our various kinetics measurements provided rate constants, listed as k_{-X} in Table 4, for a triplet decay process that leads to C−Br bond cleavage. Although these measured values actually equal the rate constant for chemical bond cleavage k_{-X} *plus* the rate constants for any competing physical decay processes, we have assumed that they represent *only* direct bond cleavage. Phosphorescence rates definitely are too slow to contribute to the observed rapid decays; but how do we justify neglect of radiationless decay? There is ample evidence that the spin−orbit coupling induced by bromine substitution increases the radiationless decay rates k_d of triplet aromatics such as naphthalene;[25] but such enhanced rate constants remain orders of magnitude lower than the measured 10^8 s^{-1} decay rates of these bromoacetophenones. The value of k_d for triplet 1-bromonaphthalene increases from 50 to 4000 s^{-1} upon raising the temperature from 77 K to ambient,[25] indicating a maximum activation energy of only 0.9 kcal/mol, far lower than the 5.3 kcal measured for these bromo ketones. We thus rule out radiationless decay as a significant competitive triplet decay process.

Quantum Yields. The model chlorovalerophenones undergo type II elimination with quantum yields in the 35−43% range common for phenyl ketones in which γ-hydrogen abstraction accounts for 100% of triplet decay. The lower values for the bromo ketones gauge the extent of competing decay reactions, which varies from 70 to 98%. The quantum yield of trapped acylphenyl radicals from **pBrB** and **pBrV** is only 17% in benzene. This value being so much lower than the percent of triplet reaction competing with γ-hydrogen abstraction means that most of the cleavage process involves reversion to the ground state of the reactant. For **mBrV**, the maximum type II quantum yield of only 25% (compared to 90% for valerophenone[26]) indicates that some 72% of the triplets cleave. The 7% yield of valerophenone again indicates great inefficiency in the cleavage reaction. As described above, we believe that these inefficiencies do not reflect direct radiationless decay of an excited state but rather represent revertible cleavage, as is common for triplet reactions and particularly noticeable for the radical cleavage of halo ketones.[27] Even though the radical pair formed by cleavage is initially in a triplet state, the spin−orbit coupling promoted by the bromine atom apparently is sufficient to allow most of the radical pairs to convert to singlets and couple before they diffuse apart to free, trappable radicals. We have noted the same effect for iodophenyl ketones.[11] In the absence of a good hydrogen source, the acylphenyl radicals add to the benzene solvent. Subsequent disproportionation of various radicals produces the acylbiphenyls that were observed as well as some dehalogenated phenyl ketone.



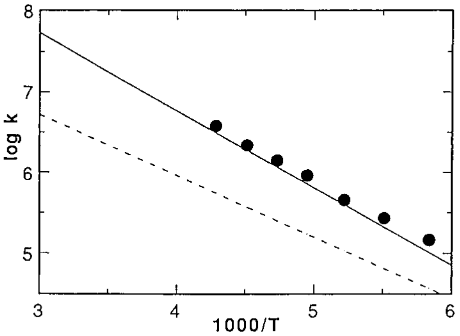


Figure 8. Arrhenius plot for decay of triplet **mBrA** corrected for competing hydrogen abstraction from methanol: (●) actual data; (- - -) $R_H = (1 \times 10^9)e^{-3200/RT}$; (—) = $1/\tau_{obs} - R_H$.

Studies on the reactivity of phenyl radicals indicate that they abstract hydrogen atoms from alkanes with rate constants on the order of 10^6 M^{-1} s^{-1}.[28] Such values are high enough for most or all of the acylphenyl radicals that have diffused away from their sibling bromine atoms to be scavenged by alkane solvent. The fact that added thiol produces slight or no increases in acetophenone yields (Figure 2) in alkane solvents, unlike the large increases produced in benzene, verifies that the acetophenone yields represent the efficiency for escape of acylphenyl radicals from the initial solvent cage. In these solvents quantum yields for reductive dehalogenation decrease with increasing viscosity in a manner consistent with recoupling of the initial caged radical pair being competitive with its diffusive separation. It is interesting how much higher the quantum yields seem to be in benzene than in alkanes of similar viscosity. The ability of benzene to complex with bromine atoms apparently can suppress recoupling of the acylphenyl radicals with bromine, certainly for those that diffuse apart and perhaps even for the original caged pair.

It is worth mentioning that thiols are known to quench triplet ketones by a charge-transfer process that normally does not generate products efficiently.[29] Fortunately, the concentrations needed to trap acylphenyl radicals are too low to measurably affect the short-lived bromoacetophenone triplets.

Cleavage Rate Constants. Both steady-state and time-resolved measurements agree that *m*-bromoacetophenone and its homologs undergo triplet state cleavage slightly faster than do the para isomers. As Figure 5 shows, both isomers of bromoacetophenone have similar activation energies; the ortho isomer appears to be similar, at least at higher temperatures. We did not determine the cause for the apparent unactivated decay process of **oBrA** at low temperature. We discuss possible causes below.

As discussed above for the bromovalerophenones, hydrogen abstraction from the solvent should be much faster for **mBrA** than for **pBrA**.[9,30] Figures 8 and 9 present Arrhenius plots for the two ketones corrected for competing hydrogen abstraction. The observed triplet decay rates were decreased by calculated rates for hydrogen abstraction from 10 M solvent, those values being $10k_H = (1 \times 10^9)e^{-(3200/RT)}$ and $(5 \times 10^8)e^{-(4000/RT)}$ for meta and para, respectively. The activation parameters for hydrogen abstraction were derived from measurements by Steel,[31] adjusted by our measurements of the effects of chloro substituents.[9] As the figures show, no correction is really needed

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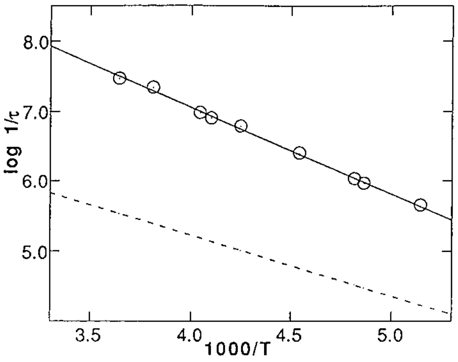

Figure 9. Arrhenius plot for decay of triplet **pBrA** corrected for competing hydrogen abstraction from toluene: (○) actual data; (- - -) $R_H = (5 \times 10^8)e^{-4000/RT}$; (—) = $1/\tau_{obs} - R_H$.

for the para isomer, but the activation parameters for the meta isomer are somewhat higher than the uncorrected data would suggest. For **pBrA**, E_a = 5.7 kcal/mol, log A = 12.0; for **mBrA**, E_a = 5.7 kcal/mol, log A = 12.4. Eyring plots produced values of $\Delta H^{\ddagger}$ = 5.3 kcal/mol for both isomers and $\Delta S^{\ddagger} = -3$ and -5 eu for **mBrA** and **pBrA**, respectively. Thus the actual differences in room temperature rates, with which the extrapolated Arrhenius plots agree well (see Table 4), seem to be due to small entropic variations, with no measurable difference in activation energies.

Thermodynamics. The latest estimates for the bond dissociation energy of bromobenzene range from 78 to 80 kcal/mol.[32] These values would appear to require activation enthalpies of at least 6−8 kcal/mol for the bromoacetophenone triplets, somewhat greater than those observed. The discrepancy probably is due mainly to the Stokes shift that we have discussed previously; the actual triplet energy of n,π* triplets is usually 1−2 kcal/mol higher than the phosphorescence 0,0 band.[33] There also may be a small error in the latest but oft-changed enthalpy of formation for phenyl radicals; or acyl substitution may lower the C−X bond energy. The latter seems unlikely, since the effect would have to be identical for ortho, meta, and para substitution. In any event, it appears that the transition state has nearly the same energy as that of the dissociated radical pair, in which case there is no activation energy for coupling of the triplet radical pair.

The triplet cleavage rates for the *m*- and *p*-bromobenzophenones are some three orders of magnitude slower than that for the corresponding bromoacetophenones. This difference amounts to an additional 4−4.5 kcal/mol of activation energy, which is exactly what would be predicted from the lower triplet energies of the benzophenones. It is noteworthy that the bromobenzophenones do not exhibit the marked isomeric differences in triplet reactivity shown by the iodobenzophenones.[11,12]

The small but measurable amount of cleavage for **pClB** is unexpected. The 10^4 s^{-1} rate constant deduced from the data would represent an activation energy of 11 kcal and thus a phenyl−Cl bond energy of 83 kcal/mol. This value is close to that formerly considered the standard.[34] One thus could view our results as evidence for lower phenyl−X bond energies. It is more likely that cleavage may be due to a small fraction of charge transfer quenching by the thiol[35] added to trap radicals, with the chlorophenyl ketone component undergoing cleavage akin to the halide ion elimination observed for radical anions.[36]

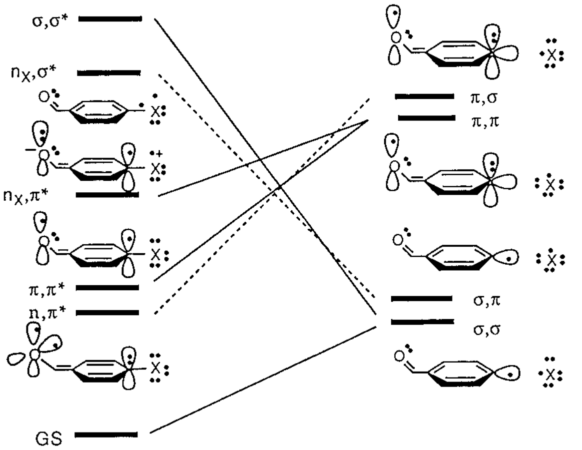

Figure 10. Natural correlation diagram between excited triplets of halophenyl ketones and radical pair cleavage products; (—) connects symmetric states; (- - -) connects antisymmetric states. n_X orbital designation is equivalent to n^{π}_{Br} in the text.

Mechanism of Cleavage. These compounds undergo concerted homolytic cleavage; what must be explained is why the bromo ketones show so little positional dependence, in contrast to the 100-fold para/meta rate ratio shown by the iodobenzophenones.[11,12] The standard interpretation of how such C−X radical cleavages occur from molecules whose lowest excited states have no σ* character invokes an activated internal conversion from a π,π* triplet to a dissociative state.[4−7] This conversion occurs on the C−X bond stretching coordinate, along which the energy of the dissociative σ* states decrease. The standard approach to determining a reaction pathway involves first constructing a correlation diagram between excited states and products and then calculating or estimating where avoided crossings between the lowest excited states and the dissociative states are the most likely. We shall do so and then examine some specific features of these reactions that favor one particular pathway for cleavage.

Figure 10 shows how the various excited states of these bromo ketones correlate by symmetry with cleavage product states. The excited states are drawn so as to show the orbitals on which the unpaired electrons are mainly localized. The n_X,σ* and σ,σ* states of halobenzenes are dissociative;[4−7] the phenyl radical can have σ or π symmetry while the bromine atom can have its unpaired electron in any of three orthogonal orbitals. Consequently the reaction is pentatopic, involving π and σ orbitals on the benzene ring and n, σ, and n^{π} orbitals on bromine. Our results obviously provide no way to distinguish among the three bromine atom symmetries. Since one p orbital on bromine is orthogonal to the σ and π systems involved in the reaction, its importance is negligible; states involving it have been omitted and we treat the reaction as tetratopic.

The ketones have either n,π* or π,π* lowest triplets, which lie within a few kcal/mol of each other in the aryl alkyl ketones; so both must be considered as "reactants". We first consider whether one is more likely than the other to convert into a dissociative state. States with π,π symmetry are connected by solid lines, and those with σ,π symmetry, by dotted lines. It was originally suggested that radical cleavages of excited states proceed by avoided crossings between states of the same overall symmetry.[37,38] In that case the π,π* triplet, which actually

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correlates with a radical pair containing an excited π-phenyl radical, would couple with a σ,σ* state that leads to a triplet pair of σ radicals. Likewise, the n,π* triplet would then couple with the n^{π}_{Br},σ* state that forms a σ phenyl radical and a π bromine atom. However, the actual cleavage of ^{3}π,π* halobenzenes has been attributed to coupling with a n^{π}_{Br},σ* state,[4−7] while we have invoked coupling of the ^{3}n,π* state with the σ,σ* state to explain the behavior of the iodobenzophenones.[11,12]

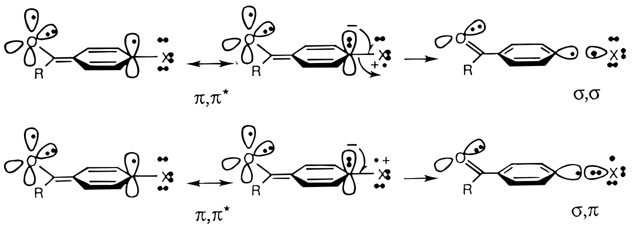
Several aspects of our results have a strong bearing on state coupling possibilities. The nearly identical activation parameters for *m*- and *p*-bromoacetophenones reflect their similar triplet excitation energies and thus indicate very similar coupling between unreactive (bound) and reactive (dissociative) states. Moreover, their n,π* and π,π* triplets have such similar 0,0 energies, both lower than that of the radical pair, that whichever one couples better with a dissociative state should drive the cleavage in all cases. (It is well established that a facile equilibrium between π,π* and n,π* triplets allows efficient hydrogen abstraction by the latter when the former are lower in energy.[21,39]) The fact that the n,π* triplets of iodobenzophenones show a large meta/para rate difference,[11,12] whereas none of the bromophenyl ketones show such a difference, strongly suggests that it is the π,π* triplets of these bromophenyl ketones that dominate the dissociation process. Put another way, it is difficult to comprehend the endothermic debromination of **mBrA** ($k = 2 \times 10^8$ s^{-1}) being faster than the exothermic deiodination of **mIBzP** ($k = 3 \times 10^7$ s^{-1}) if they both react from their ^{3}n,π* states, which are the lowest triplets for each.

The fact that *A* values for the bromoacetophenones are 10^{12} s^{-1} indicates that there is some inefficiency in the state interconversion, since the fragmentation itself inherently produces a positive entropy change. By comparison, *A* values near 10^{13} s^{-1} have been measured for α-cleavage of triplet ketones,[39] in which mixing of adjacent n and σ orbitals makes the n,π* states inherently dissociative. We suggest that the ~10-fold inefficiency for these bromo ketones should be interpreted as a low transmission coefficient κ at the transition state, caused by weak coupling and thus inefficient interconversion between electronic states of different symmetry.

In unsubstituted and most para-substituted phenyl ketones, the symmetry of the π orbitals is broken such that the lowest π* orbital has the highest coefficient at the para carbon. Thus the radical anions of benzenes with strong electron-withdrawing substituents have most of their spin and charge density at the para position, with very little meta,[40] just as observed in the n,π* triplet of benzophenone.[41] The radical anions of bromoacetophenones undergo rapid cleavage into phenyl radicals and bromide ion. This cleavage, which must be driven by the odd electron in the π* orbital, is some 100 times faster for para bromines than for meta.[36] The radical cleavage of ^{3}n,π* iodobenzophenones shows the same para/meta ratio.[11,12] Because the n orbital of the n,π* triplet is orthogonal to the π system and thus mimics an independent donor, π* electron density in the n,π* triplet is very similar to that in the radical anion.

The lowest π,π* triplets of phenyl ketones also have high unpaired electron density at the para position with very little meta.[42] Why then does the radical cleavage of these triplet bromophenyl ketones show no positional effect? If the unpaired electron density resided primarily at the para carbon in all isomers of the bromo ketones, and if it were mainly responsible for cleavage probability, it is not clear how both meta and para isomers could cleave with such similar *A* values and rates. Thus the cleavage of these π,π* triplets does not appear to be dominated by π* electron density as it is for the radical anions of the same compounds and for the n,π* triplets of the iodobenzophenones. A major difference between n,π* and π,π* triplets is that both meta and para electron-donating substituents interact very strongly with the benzoyl π system in the latter;[21] the lone pair p orbital on the halogen that is parallel to the benzene π system couples with the π system such that a degree of electron transfer from halogen to a π* orbital is mixed into the π,π* configuration to produce changes in electron density that have not been well characterized. Therefore we suggest that there is a common component of $n^{\pi}_{Br} \rightarrow \pi^*$ character mixed into the π,π* triplet of all isomers and that it is this component that allows comparable mixing with a dissociative state.

Scheme 1



If we now return to Figure 10, the symmetry-allowed conversion of a π,π* triplet into a σ,σ* state would require a double electron transfer between orthogonal orbitals, so that coupling of the two states should be weak. Such orthogonality has been deemed responsible for the low rate constants for exothermic energy transfer from n,π* triplet acetone to other ketones[43] and is well recognized as a cause of inefficient state conversions.[37,38] Interconversion with a n^{π}_{Br},σ* state involves only a single orthogonal electron transfer and forms the state thought to be responsible for the photocleavage of iodobenzene and simple alkyl halides.[6] Exact π−σ orthogonality and symmetry restrictions may be broken by the halogen moving off the axis of the phenyl−Br bond as it departs; but the final phenyl radical is σ, so the extent of such wagging may be low. Schemes 1and 2 depict these concepts as electron transfers between states and between orbitals, respectively. The surface crossings between solid lines displayed in Figure 11 are best described as only partially avoided. Although the less than optimal orbital overlap involved in both excited state interconversions could explain a low κ value, our suggestion that the n^{π}_{Br},σ* state is the one involved would mean that the bromophenyl ketone triplets react by the same mechanism suggested for iodobenzene itself,[6] both involving irreversible state conversions of π,π* triplets to a n^{π}_{Br},σ* state, which shares with the $n^{\pi}_{Br} \rightarrow \pi^*$ state an electron-deficient bromine. In that case the lack of any isomeric differences may be ascribed to this partial positive charge on bromine, which may drive the internal electron transfer strongly enough to override or to

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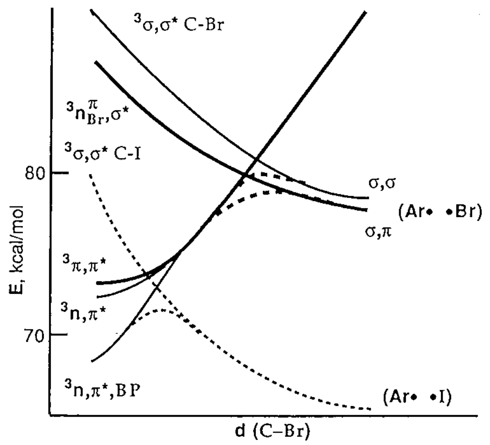
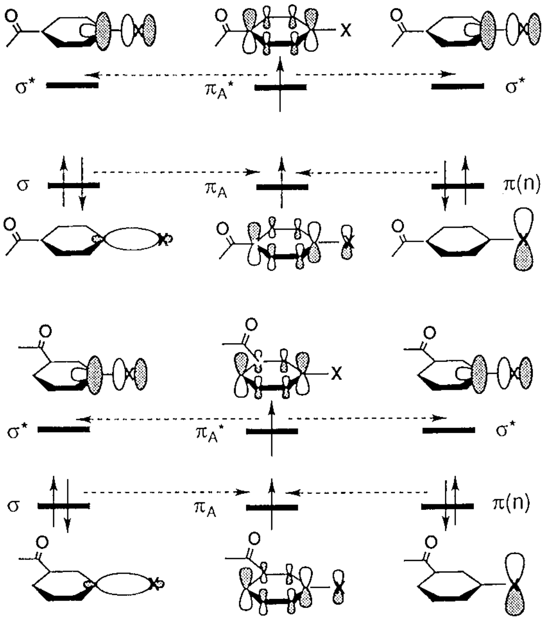


Figure 11. Potential energy diagram for activated conversion of n,π^* and π,π^* triplets of halophenyl ketones into (—) C−Br and (- - -) C−I dissociative states.

Scheme 2



change regioelectronic differences in electron density. In terms of orbital overlap, Scheme 2 indicates that significant spatial overlap occurs between the π^* and σ^* orbitals on the carbon bearing bromine, because of the $n^{\pi}_{Br} \rightarrow \pi^*$ character in the π,π^* triplet for both *m*- and *p*-bromo ketones. This overlap would facilitate conversion of the π,π^* state to either dissociative state. In contrast, there is very little overlap between the σ and π_A orbitals but strong overlap between the n^{π}_{Br} and π_A orbitals; this difference is what we believe would favor conversion to the n^{π}_{Br},σ^* state.

Figure 11 depicts a potential energy diagram for both processes, with avoided crossings between a π,π^* triplet and the two dissociative states indicated by dashed curves.[38] The various states of the bromo ketones are connected by solid lines, with the interconversion of n,π^* and π,π^* triplets shown by the former merging into the latter before intersection with a dissociative state. We could have included separate curve crossings for n,π^* triplets, but did not for the reasons stated above and because we do not know how the energy surfaces for the two bound triplets differ with respect to CBr bond stretching. Even though the bromobenzophenones have lowest n,π^* triplets, their π,π^* triplets have energies similar to those of the bromoacetophenones, lower than the phenyl−Br bond energy. Thus, as shown in Figure 11, $^3\pi,\pi^*$ states can be populated before the triplets acquire the energy required for cleavage.

We include as dotted lines in Figure 11 the reaction path previously suggested for iodobenzophenones,[11,12] in order to depict why the activation energies for endothermic cleavage of the bromoacetophenones and exothermic cleavage of the iodobenzophenones do not differ much. The endothermicity of the bromine−phenyl bond cleavage means that the lowest excited states do not intercept the dissociative state until the bond is nearly broken, such that the transition state has nearly the same energy as the product radical pair state. The iodobenzophenones intercept a dissociative state at an energy well above that of the product, so there is a significant activation energy in both directions. The behavior of the bromo ketones raises an interesting question akin to that posed by back electron transfer between radical ion pairs: what is the probability that recombination of bromine and acylphenyl radicals could generate product in a triplet state?

High Reactivity of Ortho Isomers. Each of the *o*-bromo ketones shows reactivity much higher than that of its meta and para isomers, but in different ways. The high reactivity of **oBrBzP** is entirely triplet derived and presumably reflects a steric lowering of the C−Br bond energy. If the 600-fold rate difference relative to the meta and para isomers is entirely enthalpic, it would reflect a 4 kcal/mol decrease in bond energy. The rate enhancement also could reflect a direct, through space charge transfer interaction between the bromine atom and the carbonyl, a process that is very rapid for *o*-thiyl ketones.[44] Whatever the process is, it probably is not responsible for the slow, temperature-independent decay of **oBrA**.

The unquenchable reaction of **oBrA** most likely represents some rapid cleavage from the excited singlet competing with intersystem crossing. There is precedent for such behavior in the photoenolization of *o*-alkylphenyl ketones; *o*-methylbenzophenone reacts entirely from its triplet, whereas *o*-methylacetophenone undergoes significant decay from its singlet.[45] The singlet rate constant would need to be in the range of 10^{10-11} s^{-1} and would indeed be higher than that estimated for the triplet because of the higher energy of the excited singlet and thus lower endothermicity of cleavage.

Summary. A combination of steady-state and time-resolved studies indicates that *m*- and *p*-bromophenyl alkyl ketone triplets undergo C−Br bond homolysis with 25 °C rate constants of 2×10^8 and 1×10^8 s^{-1}, respectively. The two isomers appear to have the same 5.3 kcal/mol activation enthalpy for cleavage and *A* values of 10^{12}. The $\Delta H^{\ddagger}$ value barely equals the endothermicity of cleavage as judged by the currently accepted value of 79 kcal/mol for the phenyl−bromine bond dissociation energy. The *A* values indicate some intrinsic inefficiency in triplet state cleavage, which is concluded to involve activated conversion of a π,π^* triplet into a dissociative n^{π}_{Br},σ^* state, mixing of some n^{π}_{Br},π^* character into the π,π^* state providing the requisite coupling between electronic states. The same mechanism would explain the even slower, more endothermic cleavage of triplet bromobenzophenones. In both cases the lowest n,π^* triplets are assumed to convert into π,π^* triplets before cleavage. The isomeric *o*-bromo ketone triplets cleave much more rapidly; a combination of steric acceleration and singlet state participation is suggested.

The strong dependence of cleavage product quantum yields on alkane solvent viscosity, together with the low absolute

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values, indicates that large fractions of the initially formed acylphenyl/bromine radical pairs recouple in the solvent cage in competition with diffusing apart, despite their triplet origin. Benzene minimizes this cage recombination, presumably by complexing the bromine atoms.

Experimental Section

Chemicals. Benzene solvent was commercial thiophene-free reagent grade purified by washing with sulfuric acid and then distillation from phosphorus pentoxide. Alkanes used as internal standards for GC analysis had previously been vacuum distilled and passed through alumina; the solvents were acid washed and then distilled. Naphthalene was purified by sublimation. 2,5-Dimethyl-2,4-hexadiene and 1,3-pentadiene were obtained from Chemical Samples Co.; the former was allowed to sublime in the refrigerator.

***m*-Bromovalerophenone** was prepared in 70% yield from the Grignard reagent of *m*-dibromobenzene and valeronitrile, following standard procedures including isolation of the imine salt in cold water before its hydrolysis.[46] It was purified by recrystallization from hexane, mp 43 °C: IR (KBr) 2985, 1685, 1450, 1210, 780 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.94 (t, $J = 7.5$ Hz, 3 H), 1.50 (m, 4 H), 2.86 (t, $J = 8$ Hz, 2 H), 733 (t, $J = 7.82$ Hz, 1 H), 7.67 (ddd, 8.0, 1.92, 1.08 Hz, 1 H), 7.86 (dd, $J = 7.68$, 1.42, 1.20 Hz, 1 H), 8.06 (t, $J = 1.78$ Hz, 1 H); MS *m*/*z* 242, 240, 200, 198, 185, 183, 157, 153.

***p*-Chlorobutyrophenone** was prepared by Friedel−Crafts acylation of chlorobenzene with butyryl chloride. The acid chloride was added to a slurry of aluminum chloride in chlorobenzene and allowed to stir at 0−5 °C for 1.5 h. Normal aqueous workup and distillation, followed by recrystallization from hexane, provided an 85% yield of white crystals, mp 37.0 °C: IR (KBr) 2980, 1685, 1590, 1400, 1310 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 1.00 (t, $J = 7.5$ Hz, 3 H), 1.78 (quin, $J = 7.8$ Hz, 2 H), 2.88 (t, $J = 8$ Hz, 2 H), 7.60 (AB quar, 4 H); MS *m*/*z* 184, 182, 156, 154, 147, 141, 139, 113, 11.

***p*-Bromobutyrophenone** was prepared similarly from bromobenzene in 80% yield, mp 36 °C: IR (KBr) 2980, 1685, 1400, 825 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 1.00 (t, $J = 7.5$ Hz, 3 H), 1.90 (quin, $J = 7.8$ Hz, 2 H), 2.84 (t, $J = 8$ Hz, 2 H), 7.50, 7.72 (AB quar, $J = 8.46$ Hz, 4 H); MS *m*/*z* 228, 226, 200, 198, 185, 183, 157, 155, 147.

***p*-Bromovalerophenone** was prepared similarly from bromobenzene and valeryl chloride in 80% yield, mp 36 °C: IR (KBr) 2980, 1685, 1600, 1010 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.92 (t, $J = 7.5$ Hz, 3 H), 1.50 (m, 4 H), 2.92 (t, $J = 8$ Hz, 2 H), 7.51, 7.73 (AB quar, $J = 8.46$ Hz, 4 H); MS *m*/*z* 242, 240, 200, 198, 185, 183, 157, 155.

***m*-Bromobenzophenone.** A suspension of *m*-bromobenzoic acid (5.1 g) and thionyl chloride (8 mL) in chloroform (50 mL) was refluxed for 3 h. The crude acyl chloride was dissolved in benzene (20 mL) and added dropwise to a solution of aluminum chloride (3.8 g) in benzene (40 mL). After 5 h of reflux the reaction was quenched by water and concentrated HCl. Extraction with ethyl acetate and normal workup yielded an oil which was chromatographed on a silica gel column (10% ethyl acetate in hexane) and then crystallized from methanol to give white crystals (5.3 g, 80%), mp 75−76 °C (lit.[47] mp 76−77 °C): IR (KBr) 1659, 1278 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 7.92 (t, $J = 1$ Hz, 1H), 7.77 (dd, $J = 8$, 1 Hz, 2H), 7.70 (dd, $J = 8$, 1 Hz, 2H), 7.60 (tt, $J = 8$, 1 Hz, 1H), 7.48 (t, $J = 8$ Hz, 2H), 7.36 (t, $J = 8$ Hz, 1H); ^{13}C-NMR (CDCl$_3$) δ 195.0, 139.5, 136.9, 135.2, 132.8, 132.7, 130.0, 129.8, 128.5, 128.4, 122.6; MS *m*/*z* 262 (M$^+$, 30), 260 (M$^+$, 31), 182.9 (23), 184.9 (21), 105 (100); UV (cyclopentane) λ_{max} 214 (ϵ 20 000), 249 (ϵ 17 000), 346 nm (ϵ 113).

***o*-Bromobenzophenone.** *o*-Bromobenzoic acid (5.1 g) was converted to it acid chloride, which was used to acylate benzene as described for the meta isomer. Normal workup yielded a white solid which was recrystallized from diethyl ether/hexane to afford prisms of *o*-bromobenzophenone (3.96 g, 60%), mp 40−41 °C (lit.[48] mp 41.5 °C); IR (KBr) 1663, 1292 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 7.82 (dd, $J = 8$, 1 Hz, 2H), 7.63 (dd, $J = 8$, 1 Hz, 1H), 7.59 (tt, $J = 8$, 1 Hz, 1H), 7.45 (t, $J = 8$ Hz, 2H), 7.32−7.43 (m, 3H); ^{13}C-NMR (CDCl$_3$) δ 195.7, 140.6, 136.0, 133.6, 133.1, 131.1, 130.1, 128.9, 128.5, 127.1, 119.4; MS *m*/*z* 262 (M$^+$, 13), 260 (M$^+$, 14), 184.9 (19), 182.9 (21), 105 (100); UV (cyclopentane) λ_{max} 208 (ϵ 18 000), 248 (ϵ 16 000), 343 nm (ϵ 92).

All three bromoacetophenones and *p*-bromobenzophenone were purchased from Aldrich and purified by recrystallization (para) or vacuum distillation (ortho and meta). These and the synthesized ketones were judged to be >99% pure from their NMR spectra and GC analysis.

Identification of Photoproducts. Preparative scale irradiation of **pBrV** in benzene and preparative GC isolation provided three products. Valerophenone and *p*-bromoacetophenone were identified by comparison to authentic samples; *p*-phenylvalerophenone was also identified by comparison of its spectroscopic features with those of the authentic material synthesized from biphenyl and valeryl chloride: ^{1}H-NMR (CDCl$_3$) δ 0.94 (t, 3 H), 1.52 (m, 4 H), 2.94 (t, 2 H), 7.1−8.2 (9 H); MS *m*/*z* 238, 196, 181, 152. A fourth and minor product peak was apparent on the GC traces but not isolated; it was assumed to be the cyclobutanol that always accompanies Norrish type II elimination. Photoproducts from the other ketones were readily identified by comparison to authentic samples. Dibromine was revealed by its red color. In the case of **pBrA** in cyclohexane, the reaction was followed by GC-mass spectral analysis, which revealed the presence of both cyclohexyl bromide and bicyclohexyl. GC analysis indicated a 96% yield of acetophenone and 30% of cyclohexyl bromide. The presence of HBr in the gas above the liquid sample was deduced by the color change produced on wet litmus paper. A similar experiment with *o*-bromobenzophenone gave a 92% chemical yield of benzophenone. Fluorenone as well as cyclohexyl bromide were identified by GC-MS.

Procedures. Samples were prepared and irradiated as usual.[33] Yields of products from the halo butyro- and valerophenones were measured by GC analysis. Yields of reduced ketones were measured by HPLC analysis. Phosphorescence spectra were obtained on a Perkin-Elmer MPF-44A spectrophotometer on samples 10^{-3} M in ketone, with 313-nm excitation. Flash kinetics were performed on samples ~0.005 M (o.d. ~ 0.6 cm) in 7 × 7 mm square Supracil cells fitted with serum caps that were first deaerated with nitrogen. Spectroscopic grade methanol or reagent grade toluene were used as solvents. Excitation was with a Molectron U-24 nitrogen laser (337 nm, 8 ns pulse, ~8 mJ) on J. C. Scaiano's apparatus.[49] Triplet decay was monitored at 400 or 410 nm where there was little residual absorption.

Acknowledgment. This work was supported by continuing grants from the National Science Foundation. We thank Prof. J. C. Scaiano for providing time on his flash apparatus at the NRCC and at the University of Ottawa.

JA952782F

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