

Communications to the Editor

Photoinduced Radical Cleavage of Acylphenyl Halides: Different Mechanisms for C–I and C–Br Bonds

Peter J. Wagner,* James Sedon, Carol Waite, and Anna Gudmundsdottir

Chemistry Department, Michigan State University
East Lansing, Michigan 48824

Received July 11, 1994

The photoinduced radical cleavage of carbon–halogen bonds in aryl halides is well known¹ but has received surprisingly little mechanistic study.² Molecular beam studies indicate that iodobenzene itself reacts in two stages:^{3,4} (i) an instantaneous direct dissociation, such as observed for many alkyl iodides, and (ii) a slower (~ 1 ps) cleavage, presumed to be from a π, π^* triplet, its decay rate being determined by its conversion to a π, σ^* state, in agreement with recent calculations.⁵ There have been almost no careful studies of substituted halobenzenes. Baum and Pitts⁶ reported that some halophenyl ketones undergo photoinduced C–X bond cleavage but did not measure any excited state rate constants. Since the lower triplet energies of acylbenzenes relative to those of the halobenzenes should greatly influence the kinetics of any activated bond cleavage, we have studied several iodo- and bromophenyl ketones and find that rates for triplet cleavage are $< 10^{10}$ s⁻¹ and show much different positional dependency for iodo and bromo ketones.

We have studied the meta and para isomers of the bromoacetophenones (mBrA and pBrA), the bromobenzophenones (mBrB and pBrB), and the iodobenzophenones (mIB and pIB). In all cases, UV irradiation induces C–X cleavage; the resulting acylphenyl radicals abstract hydrogen atoms from the solvent or from added thiol to yield the dehalogenated phenyl ketones. Formation of benzophenone from mBrB and pBrB barely competes with pinacol formation. However, the BrAs and IBs undergo very little triplet state hydrogen abstraction from cyclopentane; yields of dehalogenated ketones are $> 90\%$.

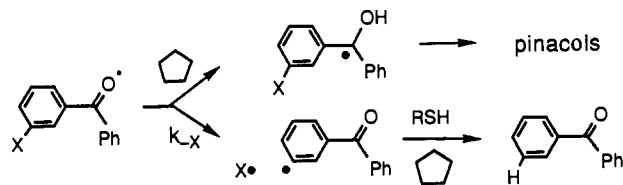


Table 1 lists photokinetics results: quantum yields of dehalogenated ketones, maximized by low concentrations of thiols;⁷ Stern–Volmer triplet quenching constants and triplet lifetimes

- (1) (a) Blair, J. M.; Bryce-Smith, D. *J. Chem. Soc. (London)* **1960**, 1788.
 (b) Kampmeier, J. A.; Hoffmeister, E. *J. Am. Chem. Soc.* **1962**, *84*, 3787.
 (c) Sharma, R. K.; Kharasch, N. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 36.
 (d) Fox, M.; Nichols, W. C.; Lemal, D. M. *J. Am. Chem. Soc.* **1973**, *95*, 8164.
 (2) The entire topic is almost entirely ignored in organic photochemistry textbooks, with the most extensive coverage (one page) provided in the following: Barltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; Wiley: London, 1975.
 (3) Dzvonnik, M.; Yang, S. *Bersohn, R. J. Chem. Phys.* **1974**, *61*, 4408.
 (4) Hwang, H. J.; El-Sayed, M. A. *J. Chem. Phys.* **1992**, *96*, 856.
 (5) Nakaoka, S.; Takemura, T.; Baba, H.; Koga, N.; Morokuma, K. *J. Phys. Chem.* **1986**, *90*, 759.
 (6) (a) Baum, E. J.; Pitts, J. N. *J. Phys. Chem.* **1966**, *70*, 2066. (b) Baum, E. J.; Wan, J. K. S.; Pitts, J. N. *J. Am. Chem. Soc.* **1966**, *88*, 2652.
 (7) Wagner, P. J.; McGrath, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 3849. Lewis, F. D.; Magyar, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 5973.

Table 1. Room Temperature Photokinetics for Various Halophenyl Ketones

ketone	$\Phi_{-X}^{\max a}$	$k_q\tau, M^{-1}$	$10^7/\tau$	$10^{-7}R_H$	$10^{-7}k_{-X}$
mBrA ^b	0.28		20 ^c		20
pBrA ^b	0.17		7 ^c		7
mBrB ^d	0.002		0.7 ^e	~ 0.7	0.01
pBrB ^d	0.003		0.6 ^e	~ 0.6	0.01
mIB	0.09 ^b	265 ^d	3.7	~ 0.7	3.0 (2.5) ^c
pIB	0.12 ^b	3 ^d	320	~ 0.6	320

^a Containing sufficient thiol (~ 0.1 M) to maximize yield of dehalogenated ketone. ^b In benzene. ^c Extrapolated from the Arrhenius plot. ^d In cyclopentane. ^e Value for comparable chloroketone in cyclopentane, ref 10.

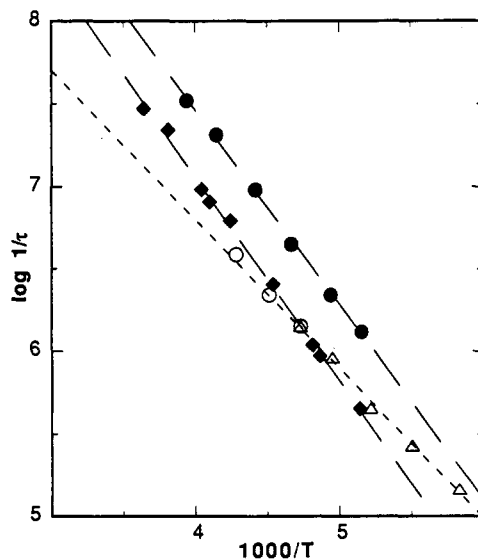


Figure 1. Arrhenius plots for triplet decay of some halophenyl ketones (uncorrected for hydrogen abstraction): ● mBrA in methanol; ◆, pBrA in toluene; ○, mIB in toluene; △, in methanol.

deduced from them,⁸ and cleavage rate constants. The latter were calculated from steady state or laser flash⁹ lifetimes, which were either multiplied by quantum yields or decreased by known rates for hydrogen abstraction.¹⁰ The low overall quantum yield indicate 70–80% in-cage coupling of the phenyl–halogen radical pairs.

Figure 1 shows Arrhenius plots for triplet decay of the BrAs and mIB between 0 and -100 °C. After correction for a few percent competing hydrogen abstraction from solvent, mBrA and pBrA share the same ΔH^\ddagger value of 5.7 kcal/mol and have log A values of 12.4 and 12.0, respectively. The similarly corrected activation parameters for mIB are 4.0 kcal/mol and 10.5. The triplet lifetime of pIB was too short for observation even at -70 °C. Since the phosphorescence of pIB and mIB at 77 K are as strong as that of benzophenone itself, k_{-X} for both must be less than the known 2×10^2 s⁻¹ rate of phosphorescence of benzophenone.¹¹ This conclusion requires that ΔH^\ddagger be ≥ 4 kcal/mol for pIB (given the 298 K decay rate) and allows us to conclude

(8) Degassed solutions 0.01–0.02 M in haloketone, containing internal standards and naphthalene as quencher or decanethiol as radical trap, were irradiated at 313 or 363 nm in parallel with valerophenone actinometers. Product yields were determined by GC analysis.

(9) Triplet–triplet absorption was excited with a nitrogen laser (337 nm); it was monitored at 400 nm for the bromoacetophenones and at 650 nm for mIB.

(10) Wagner, P. J.; Truman, R. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7093.

(11) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 136.

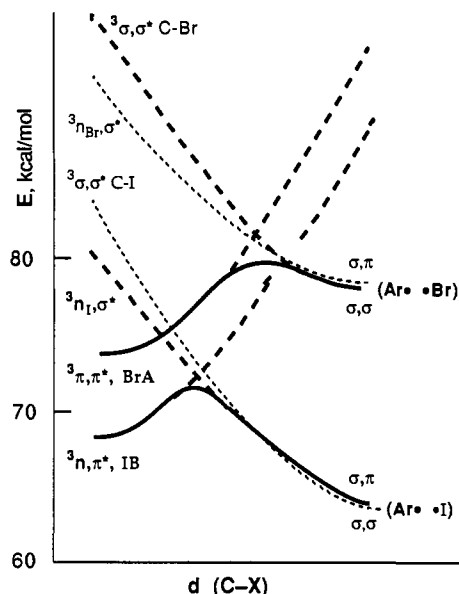


Figure 2. Potential energy diagrams for C-X bond cleavage by triplet haloketones: interactions of nondissociative states with dissociative ones of the same (—) or different (---) symmetry.

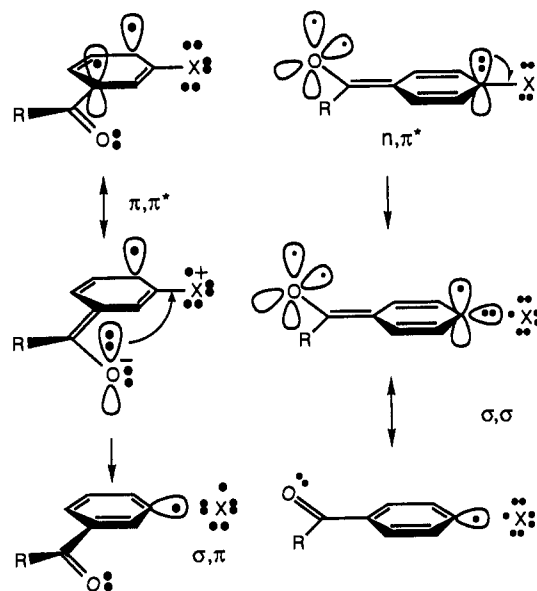
that the 100-fold rate difference between pIB and mIB is mainly nonenthalpic in origin.

The observed rate constants for cleavage are much lower than those for the plain halobenzenes;³ the difference can be related most simply to the differences in triplet excitation energies. The 77 K phosphorescence of the haloketones indicates normal triplet energies: 68–9 kcal/mol for the benzophenones; 71–2 kcal/mol for the acetophenones. The triplet energy of plain halobenzenes is 79–80 kcal/mol.¹² The most current values for phenyl-X bond energies are 78–80 kcal/mol for X = Br and 64 kcal/mol for X = I.¹³ Thus C-Br cleavage is 6–12 kcal/mol endothermic for the bromoketones, while C-I cleavage is ~4 kcal/mol exothermic. The cleavage rate constants determined for the BrBs are only 1/1000 as large as those for the BrAs and are similar for meta and para. We can safely assume that the B/A difference is entirely enthalpic, representing an extra 4 kcal/mol endothermicity, and deduce a ΔH^\ddagger value of 10 kcal/mol for both BrBs. Thus the ΔH^\ddagger values for all four types of bromoketone nearly equal the endothermicity of reaction. Figure 2 presents potential energy diagrams for cleavage that fit these observations.

The lowest π, π^* triplet of a halobenzene is not intrinsically dissociative; it has been suggested that such triplets cleave by undergoing endothermic C-X bond stretching until they become isoenergetic with and convert into a dissociative state.^{4,5} The n, π^* triplets of these haloketones likewise should not be intrinsically dissociative. Figure 2 shows avoided crossings between the lower energy "unreactive" states and dissociative states of comparable symmetry,¹⁴ which is σ, σ^* for π, π^* triplets and $n_X(\sigma), \pi^*$ or $n_X(\pi), \sigma^*$ for n, π^* triplets. However, since the two unreactive states directly correlate with excited radical pair states, the figure also contains conical intersections between states of different symmetry.

Simple cleavage reactions have positive entropies of activation. The apparent negative values for these haloketones indicate a special source of inefficiency. We believe that poor electronic coupling at the point of state interconversion is responsible for the low and variable *A* factors. In terms of transition state theory, the transmission coefficient κ in the Eyring equation is small, and state interconversion is inefficient.

Scheme 1



The question now shifts to why κ is lower for meta than for para in the iodoketones but not in the bromoketones. The difference could reflect different dissociative states for the two halogens and/or different promoting states (n, π^* or π, π^*) for the ketones. The π, π^* triplet energies of halophenyl ketones lie in the 71–74 kcal/mol range,¹⁵ while n, π^* triplet energies range from 68 kcal/mol for the benzophenones to 72–73 kcal/mol for the acetophenones.^{10,15} Given the measured activation energies, the IBs react only from their n, π^* triplets, whereas the bromoketones have both n, π^* and π, π^* triplets several kcal/mol below the measured transition states and could "react" from either. Our results suggest that π, π^* reaction dominates for the bromoketones, with better coupling between states than occurs for the n, π^* triplet of mIB.

Scheme 1 depicts the state interconversions as simple internal electron transfers from the π^* orbital to the C-X σ^* orbital, that being the actual electronic change required for σ radical formation. This π to σ electron transfer picture in fact leads to radical pair states with different symmetry than the promoting triplet, which explains low κ values. It is instructive that the strong para > meta preference of the n, π^* triplet also governs halide cleavage from haloketone radical anions.¹⁶ In both cases, cleavage seems to be driven by π^* electron density, which is much higher para than meta.¹⁷ The π, π^* triplets of halophenyl ketones are more complicated in that there is significant charge transfer to the carbonyl from both meta and para donors.¹⁵ We suggest that the partial positive charge on a meta bromine, close to the negative carbonyl, counteracts the normal higher para π^* charge density. More complete analysis will be provided in full papers.

Acknowledgment. This work was supported by NSF Grant No. CHE91-20931 and earlier awards. We thank Prof. Tito Scaiano for the use of his laser flash apparatus while he was at the NRCC in Ottawa.

(12) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; pp 95–97.

(13) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. (b) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516. (c) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(14) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(15) (a) Kearns, D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087. (b) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(16) Andrieux, C. P.; Saveant, J.-M.; Su, K. B. *J. Phys. Chem.* **1986**, *90*, 3815.

(17) E.g. Wagner, P. J.; May, M. J. *Chem. Phys. Lett.* **1976**, *39*, 350.