Hydrogen vs. electron transfer mechanisms in the chain decomposition of phenacyl bromides. Use of isotopic labeling as a mechanistic probe

Jocelyn Renaud and J.C. Scaiano

Abstract: Ring-substituted α-bromoacetophenones react with alcohols in a chain reaction leading to the corresponding acetophenone, HBr, and the carbonyl compound from oxidation of the alcohol. Two different mechanisms, involving hydrogen or electron transfer by ketyl radicals, have been proposed in order to accommodate the unusual selectivities of these reactions. By studying the efficiency of isotope incorporation from deuterated alcohols, it has been possible to determine the relative contributions from both mechanisms. For example, electron transfer dominates in the case of 2-propanol, while hydrogen transfer is more important for methanol. The results demonstrate that ring substitution in the starting ketone is not a main contributing factor in the discrimination between the two mechanisms. The only parameter that seems to be playing a major role is the nature (reducing strength) of the ketyl radicals.

Key words: dehydrobromination, charge transfer, isotope effect, ketyl radicals.

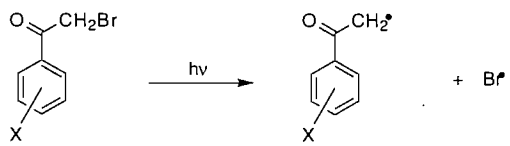
Résumé : Les α-bromoacétophénones ayant des substituants sur le cycle réagissent avec les alcools selon une réaction en chaîne pour conduire à l'acétophénone correspondante, au HBr et au composé carbonylé résultant de l'oxydation de l'alcool. Dans le but d'expliquer la sélectivité inhabituelle de ces réactions, on propose deux mécanismes différents, impliquant le transfert d'hydrogène ou d'électron par le radical cétyle. L'étude de l'efficacité de l'incorporation isotopique à partir des alcools deutériés, a rendu possible la détermination des contributions relatives des deux mécanismes. Par exemple, le transfert d'électrons domine dans le cas du 2-propanol, tandis que le transfert d'hydrogène est plus important dans le cas du méthanol. Les résultats démontrent que la présence d'un substituant sur le cycle de la cétone de départ n'est pas le facteur contributif principal dans la discrimination des deux mécanismes. La nature (force réductrice) du radical cétyle semble être, dans ce cas, le seul paramètre important.

Mots clés : déhydrobromination, transfert de charge, radicaux cétyles.

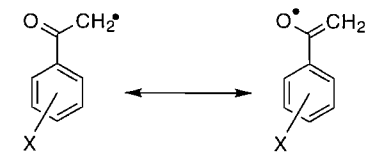
[Traduit par la rédaction]

Introduction

The photodecomposition of α-bromoacetophenone and related phenacyl bromides provides a convenient source of phenacyl radicals, reaction [1] (1–3). These radicals are readily detectable because they have a characteristic absorption band in the 500 nm region (4). Bromine atoms, the other intermediates produced in this photoreaction, are invisible in laser photolysis experiments, but their presence can be confirmed by adding complexing reagents such as benzene or bromide ions (5–7).

[1] 

While the phenacyl radical has been written as a carbon-centered species, it can also be written in its canonical form, as an oxygen-centered radical (4), i.e.,

[2] 

Recent work has suggested that the "oxy" form of this radical may account for its absorption properties (4), which are reminiscent of those recently reported for cumyloxyl radicals (8, 9). While 4-methoxyphenacyl radicals may have a spin density as a high as 0.3 at the carbonyl oxygen, their reactivity is dominated by the radical character at the carbon site (1). Product studies on the addition of phenacyl radicals to olefins show that these reactions lead to C—C bond formation, thus showing typical carbon-centered radical behavior (10, 11). Methoxyphenacyl radicals have modest reactivity; for example, the addition of the *p*-methoxyphenacyl radical to the highly reactive double bond in 1,1-diphenylethylene occurs with a rate constant of 9.4×10^7 M^{-1} s^{-1} (1). In addition, they

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J. Renaud and J.C. Scaiano.[1] Department of Chemistry, University of Ottawa, Ottawa, ON, K1N 6N5, Canada.

[1] Author to whom correspondence may be addressed. Telephone: (613) 562-5728. Fax: (613) 562-5170.

are also modest hydrogen abstractors: an example showing their low reactivity towards hydrogen abstraction is observed in various alcohol solvents and acetonitrile as solvents. Typical half-lives for the *p*-methoxyphenacyl radical in solvents such as methanol, ethanol, 2-propanol, and acetonitrile are in the neighborhood of 10 μs (1).

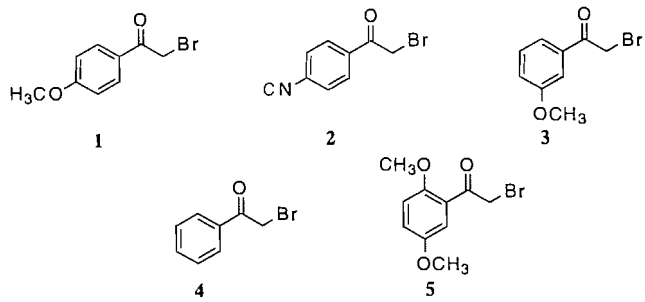
Although these carbon-centered radicals seem to be rather unreactive, our work with α-bromoacetophenones shows that steady-state irradiation in alcohol solvents leads to remarkably rapid consumption of the starting material with concomitant formation of the corresponding acetophenone. Typically, irradiation times for significant conversions are 20–50 times shorter in alcohols than in acetonitrile, thus suggesting the involvement of a chain reaction mechanism (3).

It should be noted that other bromo compounds are known to be able to carry similar chains. Chain lengths greater than 10 at temperatures between 30 and 60°C have been measured for systems studying the radical chain reaction of primary and secondary α-bromo esters by 2-propanol and 2-methyldioxolane (12). Also, using vicinal dibromides as starting materials, one can generate two bromine atoms per chain propagation step (13).

Earlier work reporting an exploratory study of this chain reaction mechanism for the dehydrobromination of ring-substituted α-bromoacetophenones in alcohols suggested a more complex mechanism than that originally anticipated (3). What seemed to be a simple electron transfer chain process turned out to be a somewhat more complex mechanism. To rationalize the unusual reactivity/selectivity of these reactions, we suggested a combination of two chain reactions involving hydrogen and electron transfer, taking place concurrently and competing for product formation. This chain reaction is mediated by the ketyl radicals derived by hydrogen abstraction from the alcohols by either the bromine atom or the phenacyl radical. In this article we make use of isotopic labeling in order to establish what fraction of the reaction proceeds by each mechanism; we combine these data with new and earlier results to provide a detailed understanding of these efficient reactions.

Our initial work on phenacyl radicals was stimulated by our interest in the photoinduced yellowing of papers manufactured from ultra-high-yield pulps. The yellowing process results largely from photoinduced reactions involving the chromophores in lignin; among these, mono- and dimethoxyphenols, methoxyacetophenones, and aryloxyanisoles are believed to play an important role (14). The absorption of light leads to various unstable intermediates, such as aromatic ketone singlets and triplets, phenoxyl, phenacyl, and peroxyl radicals, and presumably singlet oxygen. Ultimately, yellow products such as quinones, oligomers, and other degradation products are formed (14, 15). The knowledge of the kinetics and mechanisms of the reactions of unstable intermediates, particularly phenacyl radicals, should advance our understanding of lignin photochemistry in general, and ultimately lead to rational strategies to inhibit the photoyellowing of paper.

Phenacyl radicals can be produced in lignin by several reactions, including the photocleavage of structures containing the α-phenoxyacetophenone moiety. To study the behavior of this radical without the spectral and chemical interferences of the phenoxyl radical, ring-substituted derivatives of α-bromoacetophenones can be used as phenacyl precursors, where the primary photoprocess involves cleavage of the α-C—Br bond to yield the phenacyl radical and a bromine atom, reaction [1]. Ketones **1–5** are the subject of this work.



Experimental

Materials

The various substituted α-bromoacetophenones were obtained from either Lancaster or Aldrich and were recrystallized from hexane before use. Bromide ions were added as $(C_4H_9)_4NBr$ from Aldrich, which had suitable solubility in the alcohol solvents used. *n*-Dodecane was a BDH product, valerophenone; *p*-methoxyacetophenone, and *p*-cyanoacetophenone were purchased from Aldrich. Solvents were OmniSolv grade from BDH. Deuterated alcohol solvents were obtained from either Aldrich or Cambridge Isotope Laboratories.

General techniques

Competitive studies

Typical samples were 3 mL, containing 2–10 mM concentration of a ketone (**1–5**) in alcohol solvents. The samples were contained in Pyrex tubes and were deaerated (15 min) by bubbling with oxygen-free nitrogen. The samples were irradiated with two to six RPR-3500 lamps; irradiations were carried out in a "merry-go-round" apparatus to ensure that all samples received the same irradiation dose. Irradiation times varied between 1 and 5 min and were adjusted in order to obtain around 20% conversion of the starting material. Calculations of conversions were done using *n*-dodecane as an internal standard. The temperature of the irradiation chamber was in the 30–35°C range. The product ratios were analyzed by GC and (or) by GC–MS. Product identification was achieved by comparison of GC retention times with authentic samples and (or) GC–MS analysis.

Deuterium labeled product studies

Typical samples were 1 mL, containing 2 mM *para*-substituted α-bromoacetophenones in deuterated alcohol solvent. The samples were contained in Pyrex tubes and were deaerated (15 min) by bubbling with oxygen-free nitrogen. The samples were irradiated as described above. Sodium carbonate was added to each sample to prevent any acid-catalyzed isotopic exchange between the ketone product and the solvent. Substitution patterns were analyzed by GC–MS. Control samples were prepared to ensure that isotopic substitution remained intact throughout the experiment. This was done using a 2 mM solution of *p*-methoxyacetophenone in CH_3OD, CD_3OH, and

$CH_3CHODCH_3$, adding 1 mM HBr, purging for 15 min with oxygen-free nitrogen, and irradiating at 350 nm with two lamps for 2 min. The only system that did show deuterium incorporation was that involving CH_3OD as the solvent. CD_3OH and $CH_3CDOHCH_3$ were considered "clean" systems since any exchange with the solvent would not alter the substitution pattern. Control experiments using $CD_3CHOHCD_3$ were also carried out to verify that no atom transfer involving loss of hydrogen atom from the methyl group of the ketyl radical to form $CD_2{=}C(OH)CD_3$ would interfere in the deuteration pattern of the final ketone. This was done with the compounds **1** and **2** and, for both sytems, the M+1 peak was measured to be ~10%, as expected from the ^{13}C abundance. All calculations of percentage electron transfer took into consideration the natural abundance of ^{13}C, which was measured to be 9.5% (expected: 9.9% for **1–3**) using authentic samples of the corresponding acetophenones. Furthermore, no M − 1 contribution were observed for any mass spectra during this analysis.

Quantum yields

These were determined by two different experiments. In a first experiment, compound **1** was used as a starting material and the quantum yields were measured by comparing the acetophenone yields in cyclohexane with those obtained in alcohols. Irradiations were carried out at 350 nm and product concentrations determined as indicated below. The quantum yield for the primary photocleavage of the C—Br bond in cyclohexane was taken as 0.35, the same value determined earlier in methanol solvent (2). The second experiment involved using a reference system as an actinometer. Valerophenone in benzene yields acetophenone with a quantum yield of 0.30 (16). Compound **4** was used as a starting material and the quantum yields were measured in methanol, ethanol, and isopropanol. Both systems had concentrations adjusted to have an absorption of 1.5 at 350 nm. Concentrations of 25 mM for the α-bromoacetophenone system and 100 mM for the reference system were used throughout these experiments. Deaerated samples were irradiated side by side with one to six RPR-3500 lamps as described above. Irradiation times were varied between 10 s and 70 min. Calculations of conversions were done using *n*-dodecane as an internal standard. The ratios between acetophenone formation and internal standard were analyzed by GC and then plotted as a function of time. Comparing slopes between the two systems permitted measurement of chain lengths.

Gas chromatography

The competitive studies of ketone photodecomposition in alcohol solvents and quantum yield experiments using valerophenone as a reference system were quantitatively analyzed on a Perkin Elmer model 8320 capillary gas chromatograph equipped with a flame ionization detector (FID) and a DB-5 bonded-phase column of 15 m length (from J & W Scientific).

GC–MS

Analyses of samples, including those containing Bu_4NBr, were quantitatively performed on a Fisons Instruments 8000 series gas chromatograph with a capillary (DB-5, 15 m, 0.25 mm) column coupled with a MD-800 series mass spectrometer equipped with an EI ion source and a Dynolite detector, and controlled by a DEC/486 PC operating with Masslab software, release 1.12.

Cyclic voltammetry

Cyclic voltammetry measurements were carried out using a standard three-electrode cell with a glassy carbon working electrode 3 mm in diameter, a platinum coil counter electrode, and a platinum wire reference electrode in a Bu_4NBF_4 (0.1 M) – acetonitrile solution. The solvent for all measurements was distilled acetonitrile (EM Science) containing 0.1 M tetrabutylammonium perchlorate (TBAP/Fluka) as the supporting electrolyte, which was recrystallized twice from a CH_2Cl_2–ether mixture. Solutions were deoxygenated with a stream of dry argon. Measurements were made using a PAR model 173 potentiostat equipped with a PAR model 175 universal cell programmer. Voltammograms were recorded on a HP 7045B X–Y recorder. All potentials are reported with respect to the saturated calomel electrode (SCE). The voltammogram obtained for α-bromoacetophenone (**4**) at 200 mV s^{-1} showed two reduction peaks. The first cathodic peak, located at −0.78 V with respect to the saturated calomel electrode, is relevant to the irreversible reduction of compound **4**, and its height (measured with respect to the monoelectronic wave of ferrocene) corresponds to the consumption of one electron per molecule. The second peak that was observed corresponds to the reduction of acetophenone as shown by comparison with an authentic sample. The same cyclic voltammetric behavior was observed with compounds **1** and **2**. The results obtained by these experiments are summarized in Table 4 and were done at the National Research Council under the supervision of Drs. A. Houmam and D.D.M. Wayner.

Bond energy data analysis

Bond energies for the various ketyl radicals were calculated using the NIST Structures and Properties Database and Estimation Program, software version 1.1 (17).

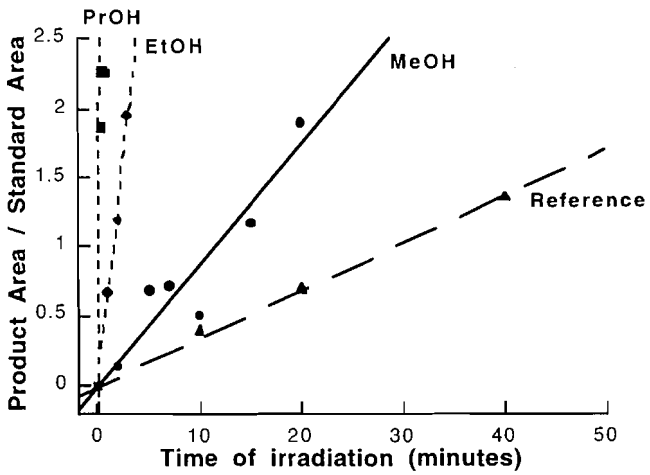
Results and discussion

It is well established that ketones **1–5** undergo efficient photodecomposition in alcohol solvents upon broad band irradiation centered at 350 nm. For example, in the case of compound **1**, the relative yields of *p*-methoxyacetophenone in various solvents were determined to be 1:4:97 for cyclohexane, methanol, and 2-propanol (3). Taking the quantum yield for the primary photocleavage of the C—Br bond in cyclohexane as 0.35 (2), the overall quantum yields are 1.4 and 34 for methanol and 2-propanol, respectively, showing a long chain in 2-propanol and a short one in methanol.

To achieve a better understanding of the chain lengths involved in these systems, valerophenone in benzene was chosen as an actinometer (16), since it gave the same photoproduct as our compound **4** in the alcohol systems of interest. Figure 1 shows the results obtained in three alcohol solvents using six UV lamps.

When comparing slopes for any given experiment with that for valerophenone (used as actinometer) one obtains relative chain lengths of 2.5 and 19 for methanol and ethanol, respectively, and a lower limit of $\geq$116 for isopropanol. In isopropanol, the conversion was so high that very short irradiation times had to be employed in order to minimize any interfer-

Fig. 1. Acetophenone yield ratios as a function of time of irradiation for valerophenone as a reference and for compound **4** in methanol, ethanol, and isopropanol irradiated with six RPR-3500 lamps.



ence from the photoproducts; exposure times were of the order of seconds as opposed to minutes for the other two solvents. Depletion of the starting material led to nonlinear production of acetophenone even after 30 sec. Taking into consideration the quantum yield of acetophenone formation of 0.30 for 100 mM valerophenone in benzene (16), values of 0.75, 5.7, and a lower limit of ≥35 were obtained as overall quantum yields of product formation. Again, short (or nonexistent) chain lengths in methanol and increasing chain lengths for ethanol and isopropanol were shown.

In a chain reaction mechanism involving photochemical initiation, the chain length is inversely proportional to the square root of the light absorbed, i.e.,

$$\text{Rate}_p \propto (\text{Rate}_i/k_t)^{1/2} \times k_p \times (\text{conc. term})$$

where the "concentration term" will usually contain one of the reactants. Rate_i is the rate of initiation. The chain length, λ, is given by:

$$\lambda = (\text{Rate}_p/\text{Rate}_i) = k_p/(\text{Rate}_i \times k_t)^{1/2} \times (\text{conc. term})$$

For a reaction initiated photochemically, the rate of initiation will be directly proportional to the light intensity absorbed (I_a) by the photoinitiator,

$$\text{Rate}_i \propto I_a$$

thus,

$$\lambda \propto 1/I_a^{1/2}$$

In a first, rather rough, approximation, I_a is proportional to the number of lamps used in the photoreactor, leading to:

$$\lambda \propto 1/(\text{no. of lamps})^{1/2}$$

To verify this mathematical relationship, the number of lamps was varied in a series of experiments. Table 1 shows the

Table 1. Chain lengths of compound **4** in various alcohol solvents.

Solvent	UV lamps	Slope ratio	Chain length
MeOH	1	5.3	1.6
i-PrOH	2	263	79
MeOH	6	2.5	0.75
EtOH	6	19	5.7
i-PrOH	6	>116	>35

results obtained in methanol and isopropanol. These results are in agreement with the mathematical relationship derived above, and therefore the chain length increased when fewer lamps were used in the photoreactor. Table 1 also includes results obtained in ethanol using six UV lamps.

It is well established that the primary photoprocess involves cleavage of the C—Br bond, as shown in eq. [1]. The radicals produced in this reaction can abstract hydrogen readily from alcohols and can initiate chain reactions by two distinct mechanisms. Schemes 1 and 2 illustrate the mechanism in the case of methanol.

Since both mechanisms involve the intermediacy of a common radical ($\cdot CH_2OH$), they cannot function as independent chains and we presume one of them will normally dominate. The final products from both reactions should be the same. Scheme 2 represents an electron transfer mechanism, which we anticipated would be favored in the case of electron-deficient molecules such as **2**. At low conversions, the reactions are quite clean, giving only the expected products.

Scheme 1. Bromine atom mechanism (hydrogen transfer).

$$Br^{\cdot} + CH_3OH \xrightarrow{k_2} HBr + \dot{C}H_2OH$$

$$\dot{C}H_2OH + ArCOCH_2Br \xrightarrow{k_3} Ar\dot{C}(OH)CH_2Br + CH_2O$$

$$Ar\dot{C}(OH)CH_2Br \xrightarrow{k_4} ArC(OH)CH_2 + Br^{\cdot}$$

$$\downarrow$$

$$ArCOCH_3$$

Scheme 2. Phenacyl radical mechanism (electron transfer).

$$ArCOCH_2^{\cdot} + CH_3OH \xrightarrow{k_5} ArCOCH_3 + \dot{C}H_2OH$$

$$\dot{C}H_2OH + ArCOCH_2Br \xrightarrow{k_6} CH_2O + H^+ + [ArCOCH_2Br]^{\dot{-}}$$

$$[ArCOCH_2Br]^{\dot{-}} \xrightarrow{k_7} ArCOCH_2^{\cdot} + Br^-$$

To distinguish between the mechanisms of Schemes 1 and 2, experiments were carried out in the presence of 10 mM bromide ions, added as Bu_4NBr. We assumed that the mechanism of Scheme 1 would be heavily influenced, since bromine atoms form the less reactive intermediate $Br_2^{\dot{-}}$ by complexation with bromide, i.e., (6, 13, 18),

$$[3] \quad Br^{\cdot} + Br^- \rightleftharpoons Br_2^{\dot{-}}$$

We found that in methanol solvent, addition of bromide ion caused a 4.5 times decrease in product formation in the case of **1**, but this was reduced to only a factor of 2.0 in the case of **2**.

These results suggest that the bromine atom mechanism must be dominant for **1** and possibly plays a role even in the case of the electron-deficient cyano-substituted compound **2**.

To determine the relative reactivity of ketones **1–5** towards ketyl radicals, we carried out a series of competitive experiments in which ketones **1–5** were irradiated in pairs, and the ratio of products was examined for various ratios of starting materials. The product ratio for ketones **A** and **B** is related to the ratio of precursors according to:

$$[4] \quad \frac{\phi_A}{\phi_B} = \frac{k_r^A}{k_r^B} \frac{[A]}{[B]}$$

where k_r^A and k_r^B represent the values of k_3 and k_6, since these are the only steps in which the two ketones compete for reaction with the ketyl radical, i.e.,

$$[5] \quad k_r^A = k_3^A + k_6^A$$

Clearly, product formation in both reaction schemes is determined by reaction of the ketyl radicals with the α-bromoacetophenones, regardless of which one is the predominant mechanism.

Figure 2 shows plots according to eq. [4] for representative pairs of ketones in methanol, while Fig. 3 shows the corresponding plots for **1** and **2** in methanol, ethanol, and 2-propanol. The values of k_r^A/k_r^B obtained from these studies have been summarized in Table 2. The *para*-substituted ketones follow the anticipated order of reactivity according to their electron-accepting ability, i.e., *p*-CN > *p*-H > *p*-CH_3O.

We were surprised by the results for **1–2** mixtures in the different alcohols. These results (see Table 2) show that the selectivity order is 2-propanol > ethanol > methanol. Assuming that the better reducing agent (2-propanol) will react faster, one would have anticipated the lowest selectivity in this case.

The fact that **1** is less reactive than **2** suggests that the reaction is not in the Marcus inverted region since the kinetics follow the normal dependence on driving force (19, 20), A more likely explanation for the unusual selectivity–structure dependence is that the hydrogen transfer mechanism of Scheme 1 is intrinsically less selective than the electron transfer process of Scheme 2. Further, we anticipate that the mechanism of Scheme 1 will be more likely to be favored over Scheme 2 in the case of methanol than for 2-propanol. This rationale is based on our analysis of bond energy data for the various ketyl radicals, where reaction [6] is not very sensitive to the detailed substitution pattern.

$$[6] \quad R^1R^2\dot{C}OH \longrightarrow R^1R^2CO + H$$

The ΔH_r for reactions is 30.3, 27.7, and 27.2 kcal/mol for the radicals from methanol, ethanol, and 2-propanol, respectively (17).

A quantitative approach to discriminating between these two schemes is to utilize deuterium-labeled alcohols, since both reaction pathways should give a distinct isotopic pattern. Under such isotopic labeling conditions, Schemes 1 and 2 would yield the same product, acetophenone, with one unit mass difference, and Schemes 3 and 4 show the reaction products for the case of compound **1** in CD_3OH.

Fig. 2. Dependence of product ratios following 350 nm irradiation of **1/2** (●) and **4/2** (■) mixtures in methanol.

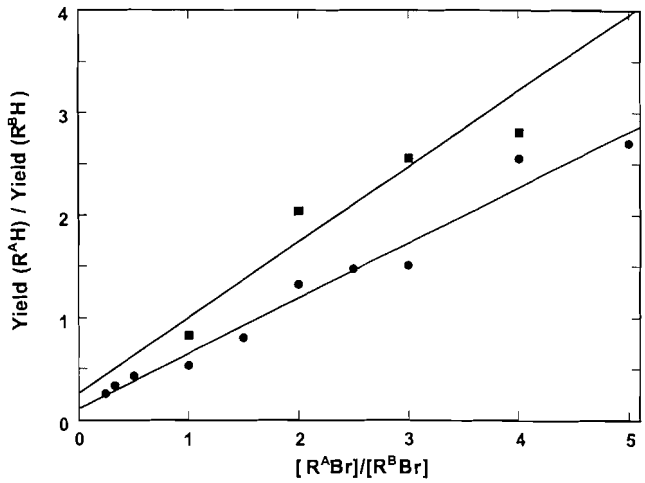


Fig. 3. Dependence of the product ratios following 350 nm irradiation of **1/2** mixtures in methanol, ethanol, and 2-propanol.

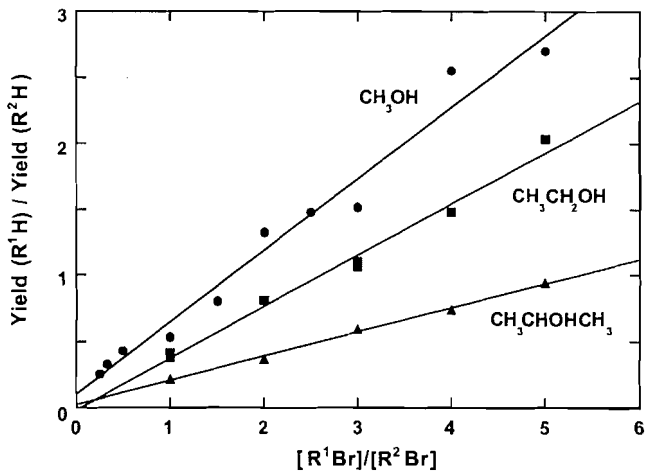


Table 2. Competitive studies of ketone photodecomposition in alcohol solvents at room temperature

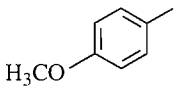
Substrates			
A	B	Solvent	k_r^A/k_r^B
1	2	Methanol	0.54
1	3	Methanol	1.68
4	2	Methanol	0.74
3	5	Methanol	0.52
1	2	Ethanol	0.39
1	2	2-Propanol	0.18
4	2	Ethanol	0.67
4	2	2-Propanol	0.35

Scheme 3. Bromine atom mechanism.

$$Br^{\bullet} + CD_3OH \xrightarrow{k_2} DBr + \dot{C}D_2OH$$

$$\dot{C}D_2OH + ArCOCH_2Br \xrightarrow{k_3} Ar\dot{C}(OH)CH_2Br + CD_2O$$

$$Ar\dot{C}(OH)CH_2Br \xrightarrow{k_4} ArC(OH)CH_2 + Br^{\bullet}$$

Ar =  $ArCOCH_3$ $m/z = 150$

Scheme 4. Phenacyl radical mechanism.

$$ArCOCH_2^{\bullet} + CD_3OH \xrightarrow{k_5} ArCOCH_2D + \dot{C}D_2OH \quad (m/z) = 151$$

$$\dot{C}D_2OH + ArCOCH_2Br \xrightarrow{k_6} CD_2O + H^+ + [ArCOCH_2Br]^{\dot{-}}$$

$$[ArCOCH_2Br]^{\dot{-}} \xrightarrow{k_7} ArCOCH_2^{\bullet} + Br^-$$

Table 3 shows the percentage of electron transfer measured for compounds **1** and **2** in *three* different deuterated alcohol solvents. The choice of substrates permitted study of both extremes of the electron-accepting capability of the *para*-substituted family, and the choice of alcohols permitted study of both extremes of the electron-donating capability of the ketyl radicals.

The percentage of electron transfer was determined by measuring and comparing the intensity (%TIC) of the molecular ion peaks corresponding to the parent and the mono-deuterated acetophenones. A measured natural abundance of ^{13}C of 9.5% was taken as the correction factor for adjusting these peaks. For example, the system studying the photochemistry of compound **1** in CD_3OH was analyzed as follows:

Product formation resulting from Scheme 3 gives a molecular ion peak of 150. Correcting for the ^{13}C content, the molecular ion peak now corresponds to:

$$M_{150} = M_{150\,(exp.)}\,(1 + 9.5\%)$$

Product formation resulting from Scheme 4 gives a molecular ion peak of 151. Correction of this peak corresponds to:

$$M_{151} = \{M_{151\,(exp.)}\,(1 - (M_{150\,(exp.)} \times 9.5\%))\} \times (1 + 9.5\%)$$

where the last multiplying factor takes into consideration the ^{13}C abundance present in the mono-deuterated peak.

Therefore the percentage of electron transfer (%et) is given by the following relationship:

$$\%et = M_{151} / (M_{150} + M_{151}) \times 100\%$$

and consequently the percentage of hydrogen transfer (%Ht) is given by:

$$\%Ht = 100\% - \%et$$

Clearly, these results demonstrate that the nature of the starting material is not a main contributing factor in the discrimination between the two schemes. The only parameter that seems to be playing a major role is the nature (reducing strength) of the ketyl radicals.

Table 3. Percent of electron transfer measured for compounds **1** and **2** in various deuterated alcohol solvents (^{13}C corrected).

Compound	CD_3OH	$CH_3CDOHCH_3$	$CH_3CHODCH_3$
1	21	81	96
	23	85	98
	22	77	96
Average	22	81	97
2	23	88	96
		89	94
		87	93
		82	
Average	23	86	94

Table 4. Reduction potentials[a] for compounds **1**, **2**, and **4** in acetonitrile – 0.1 M TBAP at 25°C, reported with respect to the saturated calomel electrode (SCE).

Compound	E (RBr / R·Br$^-$) V vs. SCE
1	−0.78
2	−0.68
4	−0.78

[a]Estimated irreversible reduction potentials, see experimental section.

Because of isotope effects, one can anticipate that the hydrogen transfer step in the overall mechanism (k_3) will be the one that is going to be influenced the most by the nature of the deuterated solvent. This effect will explain the differences in percentage of electron transfer between the two isopropanol solvents. In the case of $CH_3CHODCH_3$, that step is slowed down to the degree of being unable to compete anymore with the electron transfer step (k_6) and therefore we observe near-quantitative electron transfer for that system.

Cyclic voltammetry experiments were performed on the *para*-substituted family in order to verify that the starting material is an unimportant parameter in the overall chain reaction mechanism. Table 4 summarizes the results obtained for the reduction potentials measured in acetonitrile. These results are in agreement with the previous statement that the nature of the substrate is of little consequence in determining the reaction pathway chosen during the photodecomposition.

Conclusion

In conclusion, the photoinitiated reaction of ring-substituted α-bromoacetophenones with alcohols involves an efficient chain reaction leading to the corresponding acetophenone, HBr, and the carbonyl compound from oxidation of the alcohol. Two different mechanisms, involving hydrogen or electron transfer by ketyl radicals, were proposed in order to accommodate the unusual selectivities of these reactions. Studies of isotope incorporation from deuterated alcohols leads to the conclusion that electron transfer (Scheme 2) dominates in the case of 2-propanol, while hydrogen transfer (Scheme 1) is most important for methanol.The results demonstrate that ring substitution in the starting ketone is not a main contributing factor in the discrimination between the two

mechanisms; the observation is further corroborated by the relatively minor variations observed (see Table 4) in the reduction potentials. The only parameter that seems to be playing a major role is the nature (reducing strength) of the ketyl radicals.

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