JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2000; **13:** 634–639

Aryl substituent effects and solvent effects on the decarbonylation of phenacetyl radicals

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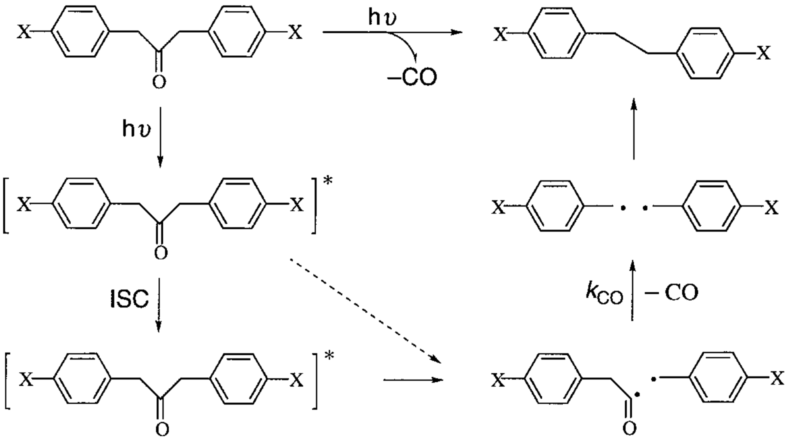
Received 13 December 1999; revised 22 February 2000; accepted 7 March 2000

ABSTRACT: Five aryl-substituted phenacetyl radicals (X = *p*-MeO, *p*-Me, H, *p*-Cl, *p*-CF_3) were generated by laser photolysis of the corresponding dibenzyl ketones in *n*-hexane and acetonitrile. The decarbonylation reaction was monitored through the rise in time-resolved absorption of the benzyl radical chromophore at 317 nm. The decarbonylation rate constants were obtained by a numerical integration procedure, where second-order radical reactions were explicitly taken into account. Values of (2–3) $\times 10^6$ s^{-1} in acetonitrile and (6–10) $\times 10^6$ s^{-1} in *n*-hexane revealed a large solvent effect for all derivatives (by a factor of $\sim$3). The electronic substituent effect indicates that both electron-withdrawing and electron-donating *para* substituents accelerate the decarbonylation slightly. The rate constants followed the order MeO $>$ Me, Cl, CF_3 $>$ H. The substituent effects are interpreted in terms of the ability of the *para* substituent to stabilize the benzyl radical resulting from decarbonylation. Evidence for a polar effect was not obtained. The underlying reasons for the observed solvent effect are discussed. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: phenacetyl radicals; decarbonylation; aryl substituent effects; solvent effects

INTRODUCTION

The decarbonylation of acyl radicals in solution has been extensively examined owing to its importance in photochemistry, e.g. in the Norrish Type I cleavage, and in radical chemistry, e.g. for the development of radical clocks.[1–10] Photocleavage of dibenzyl ketones, for example, proceeds through phenacetyl radicals (Scheme 1). Photolysis produces a singlet-excited state with a lifetime of ca 3 ns,[11] which undergoes intersystem crossing to the triplet state, along with fluorescence and some cleavage.[12] The triplet state cleaves efficiently and fast (<0.1 ns) to one benzyl and one phenacetyl radical.[3] The decarbonylation step is slower (ca 100–500 ns) and produces a second equivalent of benzyl radicals,[4,5] which ultimately undergo radical coupling to produce predominantly diphenylethane.[2] The latter two reactions can be directly monitored through the time-resolved transient absorption of the benzyl chromophore.[4,5] In the present work, we employed the photolysis of *para*-substituted



Scheme 1

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Contract/grant sponsor: Swiss National Science Foundation.
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dibenzyl ketones to generate a series of aryl-substituted phenacetyl radicals to evaluate electronic substituent effects and solvent effects on the decarbonylation process.

This study complements previous work on geminal substitution in phenacetyl radicals,[5,8] solvent effects on the decarbonylation of the parent phenacetyl radical[4,9,13] and the corresponding activation energy.[4,5,11] It is noteworthy that a study of aryl substituent effects has been initiated previously but the data set, which contained *p*-MeO, *p*-*t*Bu and *p*-Br as substituents in isooctane as solvent, was considered too small to draw definite conclusions.[8] We selected *p*-CF_3 and *p*-Cl as electron-accepting substituents and *p*-Me and *p*-MeO as electron donors in two solvents, *n*-hexane and acetonitrile. This choice of substituents is restricted but it must be kept in mind that phenacetyl radicals containing strongly electron-withdrawing groups such as nitro and cyano cannot be generated by photolysis of dibenzyl ketones.[1]

EXPERIMENTAL

Materials. The substituted dibenzyl ketones (*p*-MeO, *p*-Me, *p*-Cl, *p*-CF_3) were synthesized according to reported procedures.[14–16] They were purified by recrystallization and characterized by melting point, NMR (^{1}H and ^{13}C) and GC–MS. The parent dibenzyl ketone (Fluka) was purified by sublimation. The solvents were obtained from Scharlau (Switzerland) in the highest quality. All experiments were performed at ambient temperature (ca 24 °C)

Spectroscopic measurements. A XeCl excimer laser pulse from a Lambda Physics EMG laser (308 nm, FWHM ca 20 ns, pulse energy 80–120 mJ) was used for excitation in the laser-flash photolysis experiments. The samples were degassed by three freeze–pump–thaw cycles in laboratory-made quartz cells. The transient absorption around 317 nm was used to monitor the decarbonylation of the phenacetyl radicals and the kinetic traces were registered by means of a transient digitizer. Data accumulation was not required. The decarbonylation rate constants were extracted from the decay traces by non-linear fitting using a numerical integration procedure with the program Profit 5.1.2 (Quantum Soft, Zürich, Switzerland).

RESULTS

The photochemical behavior of dibenzyl ketones has been the subject of numerous previous investigations.[1–9] The quantum yield for diphenylethane formation is about 0.6–0.8 for most dibenzyl ketones,[1,3,12] except for derivatives with strongly electron-withdrawing groups (*p*-CN and *p*-NO_2), which do not undergo this photoreaction efficiently (quantum yield <2%). This is known for the *p*-CN derivative[1] and was confirmed in this work for the *p*-NO_2 derivative; higher energy excitation (248 nm) was also employed in the present work, but did not produce significant yields of the *p*-CN and *p*-NO_2 substituted benzyl radicals. Triplet energy transfer from the ketone moiety to the *p*-CN- or *p*-NO_2-substituted aryl groups appears to be responsible.[1]

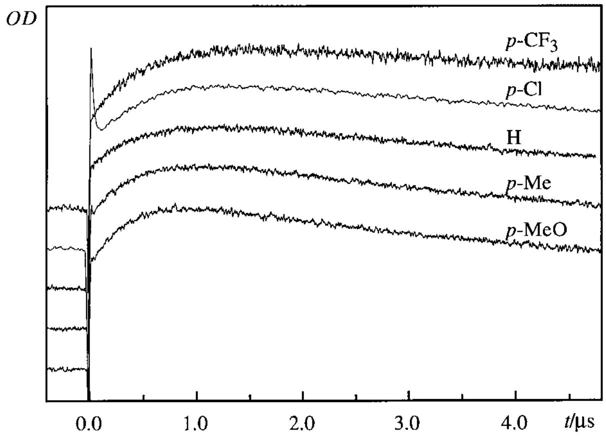

Figure 1. Substituent effect on the decarbonylation process of phenacetyl radicals in acetonitrile. The *OD* scale is linear, but the traces are normalized to the same intensity, since no clear substituent effect on the signal intensity was observed

Upon excitation with a 308 nm laser pulse, the dibenzyl ketone precursors gave transient absorptions around 317 nm, the $2^2A_2 \longleftarrow X^2B_2$ absorption band of the benzyl radical chromophore.[6,17] Dissociation of dibenzyl ketone triplets is known to be fast[3] and generally occurs within the duration of the laser pulse, producing one equivalent of benzyl radical.[4,5] This results in an initial 'step' feature in the decay traces (Fig. 1). An exception is the *p*-Cl derivative, where a fast initial decay (ca 20 ns) is observed (Fig. 1). This is tentatively attributed to the triplet-excited *p*-Cl dibenzyl ketone, which may undergo the cleavage process more slowly than the other derivatives and which should absorb in this region, akin to simple aliphatic ketones.[18,19] The step in the absorption is followed by a time-resolved rise (Fig. 1). This is attributed to the decarbonylation reaction, which produces another equivalent of benzyl radicals.[4,5] On longer time-scales, the benzyl radical absorption depletes with second-order kinetics,[6,9,20] when oxygen is excluded.[11] This reaction corresponds to benzyl radical coupling,[2] which is known to be a diffusion-controlled reaction.[6,9,20] A clear dependence of the signal intensity on the *para* substituent was not recognized (cf. normalized traces in Fig. 1). This is in agreement with the observed constancy of the decomposition quantum yields of several substituted dibenzyl ketones.[1]

The essential quantitative information from the decay traces is the decarbonylation rate constant, k_{CO}, in

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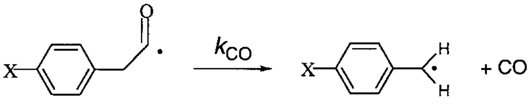
Scheme 2. In limiting cases, when the decay of the benzyl radicals is slow and a plateau is reached, this unimolecular rate constant can be directly obtained by fitting a monoexponential rise function to the transient data.[4,5,8–10] In practice, this limitation requires low laser pulse energies.[5,8] The resulting traces are weaker, but display the desired plateau region, since the concentration of radicals and, thus, the observed bimolecular rate constants are small.



Scheme 2

Ideally, the step and rise feature should have the same height when a plateau is reached, but it turns out that the height of the rise is always smaller (typically 10–40%) than the step. This has been noted previously.[4] Since this discrepancy obtains upon extrapolation to zero time (center of laser pulse), the effect must be real. Acetyl radicals, including phenacetyl radicals, display absorption near 320 nm[10,22] and this may account for the above observation. In addition, some phenacetyl radicals, which are known to undergo photoinduced decarbonylation,[21] and also some excited dibenzyl ketone molecules may absorb a second photon within the laser pulse and undergo ‘direct’ decarbonylation, which is known for aliphatic ketones.[22]

To allow a more accurate data analysis, second-order radical reactions should be explicitly taken into account. This was achieved by non-linear fitting of a numerically integrated system of the differential functions

$$\frac{d[\mathrm{Bz}]}{dt} = -2k_1[\mathrm{Bz}]^2 - k_2[\mathrm{Bz}][\mathrm{BzCO}] + k_{\mathrm{CO}}[\mathrm{BzCO}] \qquad (1)$$

$$\frac{d[\mathrm{BzCO}]}{dt} = -2k_3[\mathrm{BzCO}]^2 - k_2[\mathrm{Bz}][\mathrm{BzCO}] - k_{\mathrm{CO}}[\mathrm{BzCO}] \qquad (2)$$

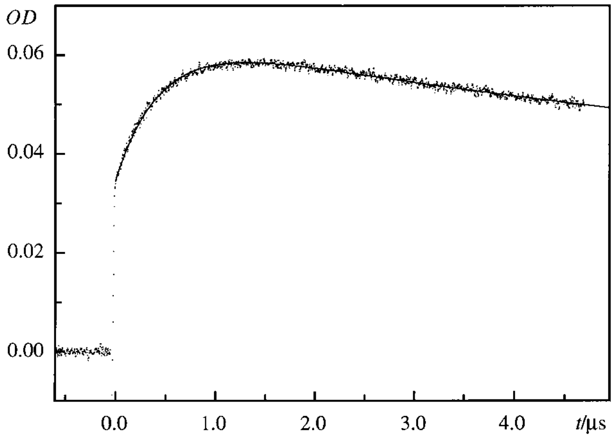


Figure 2. Transient absorption decay trace of the parent dibenzyl ketone in acetonitrile. Shown are the experimental data points and the corresponding non-linear fit obtained by numerical integration of the system of coupled differential Eqns (1) and (2)

to the data. Here, [Bz] is the concentration of benzyl radicals which is being monitored and [BzCO] is the concentration of the phenacetyl radicals. The initial concentrations of these two intermediates were *not* set equal as was done in previous work,[11,13] in keeping with the observed different heights of the step and rise features (Fig. 1). The rate constant for radical–radical coupling involving benzyl and phenacetyl radicals (k_1, k_2, k_3) were set equal for the fitting, i.e. $k_1 = k_2 = k_3$, since radical coupling of carbon-centered radicals, even coupling of two resonance-stabilized benzyl radicals, is generally fast and close to the diffusion-controlled limit (subject to a spin-statistical factor).[6,13] The fitting procedure afforded the decarbonylation rate constants k_{CO} which are compiled in Table 1. Excellent fits were obtained, as illustrated in Fig. 2. Direct monoexponential fitting (see above) to the same traces produced apparent decarbonylation rate constants which were consistently higher (up to 50%) than those obtained from the numerical integration procedure. Furthermore, the kinetics was examined both in *n*-hexane and acetonitrile and a significant solvent effect was observed (Table 1 and Fig. 3).

Table 1. Dependence of the decarbonylation rate constants (k_{CO}) of phenacetyl radicals in *n*-hexane and acetonitrile on the *para* substituent X and polar and radical substituent constants

	k_{CO} (10^6 s^{-1})[a]			
X	*n*-Hexane	Acetonitrile	σ_{pol}[b]	σ_{rad}[c]
p-OMe	9.9	3.1	−0.27	0.24
p-Me	7.3	2.5	−0.17	0.11
H	6.4	2.0	0.00	0.00
p-Cl	7.4	2.4	0.23	0.12
p-CF_3	6.8	2.3	0.54	0.08

[a] Error in data is 10%.
[b] Polar substituent parameter from Ref. 23.
[c] Radical substituent parameter from Ref. 25.

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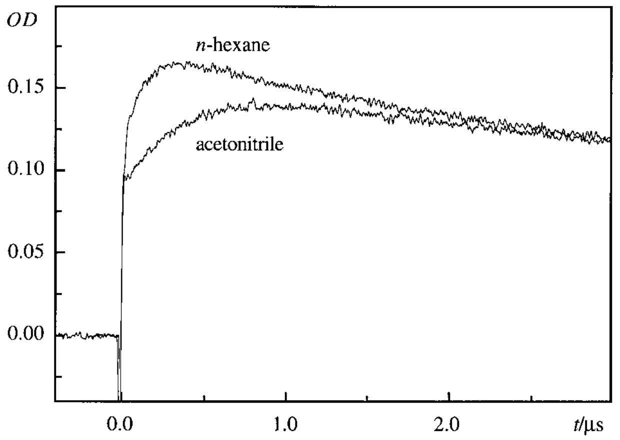


Figure 3. Solvent effect on the decarbonylation process of the *p*-OMe-substituted phenacetyl radical

Our present rate data are generally in good agreement with previous measurements. They tend to be lower than some of the original data,[4,8] which may be systematically related to the different data analysis. Noteworthy, the agreement with another study on the parent phenacetyl radical, in which explicit correction for the radical recombination reactions was also made,[13] is excellent, i.e. within the error limit. Our rate constant for the parent phenacetyl radical in *n*-hexane (6.4×10^6 s^{-1}) falls between the previous values in alkane solvents [(5.3–$9.1) \times 10^6$ s^{-1}].[4,5,10,13] The reported decarbonylation rate constant in isooctane for the *p*-MeO derivative (15×10^6 s^{-1})[8] is larger than our value in *n*-hexane (9.9×10^6 s^{-1}), but the literature data[8] for the *p*-Br (7.2×10^6 s^{-1}) and *p*-*t*Bu derivatives (10×10^6 s^{-1}) in isooctane are the same or higher than our *n*-hexane values for the closely related substituents *p*-Cl (7.4×10^6 s^{-1}) and *p*-Me (7.3×10^6 s^{-1}). With respect to the effect of the solvent, our value for the parent phenacetyl radical in acetonitrile (2.0×10^6 s^{-1}) lies between those determined in previous studies in the same solvent (1.7×10^6 and 4.5×10^6 s^{-1}).[10,13] Regardless of the significant variation of the absolute data in acetonitrile, all studies confirm a slower reaction in acetonitrile than *n*-hexane. The decarbonylation rate constant was also determined in ethanol for the *p*-MeO derivative (7.8×10^6 s^{-1}). As found previously for the parent compound, where values of (5.2–$2.5) \times 10^6$ s^{-1} were found in alcohols,[4,13] the trend of the solvent effect on the rate constant for decarbonylation is consistent and follows the order alkanes > alcohols >acetonitrile.

Fluorescence emission of the dibenzyl ketones has been described as an experimental complication in previous measurements.[4,9,13] Indeed, fluorescence emission was also observed in our experiments, strongest for the methoxy derivative. However, complications arising from luminescence depend sensitively on the technical details of the experimental set-up, most importantly the photomultiplier response and the focus and also the pathlength of the monitoring beam. In our experiments, adverse effects of fluorescence could be avoided by focusing the monitoring beam accurately through a small iris. Hence fluorescence caused no major complications with the data analysis in our experiments, and correction for luminescence (which itself may introduce a systematic error) was not required.

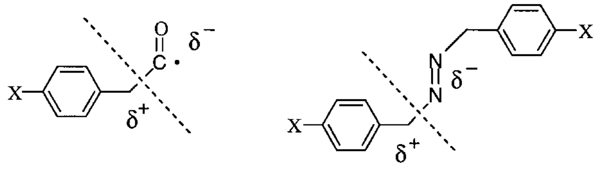
DISCUSSION

Substituent effects

Some *para* substituents have already been examined in a previous study, but it was noted that the data were too limited to draw definitive conclusions.[8] The previous measurements were carried out in the non-polar isooctane and a direct monoexponential fitting was applied. Our study adds three new substituents and includes the most strongly electron-withdrawing substituent examined to date (*p*-CF_3).

The rate constants for decarbonylation (k_{CO}) of substituted phenacetyl radicals are of the order of (2–$3) \times 10^6$ s^{-1} in acetonitrile and (6–$10) \times 10^6$ s^{-1} in *n*-hexane. The dependence on the substituent X follows the trend MeO > Me, Cl, CF_3 > H. We consider the observed substituent effects significant owing to the observation in two different solvents with considerably different rate constants and owing to the refined data analysis employed (numerical integration).

The present data (and also the previous measurements)[8] suggest that both electron-donating substituents such as *p*-MeO, *p*-Me, and *p*-*t*Bu and electron-withdrawing groups such as *p*-Cl, *p*-Br and *p*-CF_3 accelerate the decarbonylation. This demonstrates that a polar effect is not dominant, cf. Hammett σ values[23] (σ_{pol} in Table 1). Rather, the observed dependence is diagnostic for a radical-stabilizing effect, since both electron-donating and -withdrawing *para* substituents are known to stabilize the benzylic radicals,[24] which are being produced by decarbonylation (Scheme 2). Indeed, the Creary scale for radical substituent effects,[25] which we have employed in the quantitative analysis of the deazatization rate constants of phenylazomethanes (right-hand in Scheme 3),[26] predicts the selected aryl substituents to be radical stabilizing (cf. positive σ_{rad} values in Table 1); the *p*-CF_3 group displays the weakest radical-stabilizing effect.[24] A linear correlation of $\log(k^X_{CO}/k^H_{CO})$versus σ_{rad} applies in both solvents ($n = 5$, $r > 0.97$).



Scheme 3

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Table 2. Calculated dipole moments of substituted phenacetyl radicals and the corresponding benzyl radicals resulting from decarbonylation

	μ(D)[a]		
X	Phenacetyl radical[a]	Benzyl radical[a]	$\Delta\mu$(D)[b]
p-OMe	2.86	1.29	−1.57
p-Me	2.66	0.33	−2.33
H	2.54	0.03	−2.51
p-Cl	2.25	0.12	−2.13
p-CF_3	3.16	3.37	0.21

[a] Calculated with the UHF–AM1 method[30] with the program MacSpartan Plus (Wavefunction).

[b] Difference in calculated dipole moment between the benzyl radical and phenacetyl radical.

The comparison with the deazatization of phenylazomethanes[26] is instructive since the bonds being broken have the same polarization (Scheme 3). Interestingly, radical effects are dominant in both reactions, although a small but significant polar effect of ca 20% was detected in the thermolysis of the phenylazomethanes. Namely, the ratio of the radical and polar reaction constants obtained from a two-parameter Hammett treatment, i.e. ρ_{rad}/ρ_{pol}, was 3.6.[26] This polar effect was attributed to a ground-state stabilization,[26] which arises from the action of the substituents on the strength of the polar bond.[27,28] A similar polar effect is expected for the decarbonylation, but the data set is too small and displays insufficient variation to separate a potential polar effect from the larger radical effect. In fact, a two-parameter Hammett treatment[26] revealed that the inclusion of a polar contribution (σ_{pol}) does not improve the correlation between $\log(k^{X}_{CO}/k^{H}_{CO})$and σ_{rad} significantly.

The dominance of radical-stabilizing substituent effects in the decarbonylation of phenacetyl radicals and the previous, more general observation[7] of an Evans–Polanyi relationship in the decarbonylation of acyl radicals suggests that the kinetics of decarbonylation should be correlated with the reaction enthalpy, i.e. the bond dissociation enthalpy (BDE) of the C—CO bond being broken. The UHF–AM1 method[29] with the program MacSpartan Plus (Wavefunction) was employed for the calculation of the BDEs of the phenacetyl radicals, including the necessary correction for zero-point vibrational energies. Although the simple AM1 method produces the absolute value of the BDE of the parent phenacetyl radical poorly [cf. calculated BDE of $+64\ \mathrm{kJ\ mol^{-1}}$ versus $-(6 \pm 2)\ \mathrm{kJ\ mol^{-1}}$ estimated otherwise],[7] the relative values (ΔBDE) may nevertheless be meaningful. The calculated data indicate a decrease in BDE for the substituted phenacetyl radicals relative to the unsubstituted case (X = H), namely for X = *p*-MeO ($\Delta\mathrm{BDE} = -1.6\ \mathrm{kJ\ mol^{-1}}$), *p*-Me (−0.8), *p*-Cl (−2.5) and *p*-CF_3 (−2.2). This supports qualitatively the idea that both the electron-accepting and the electron-withdrawing substituents weaken the bond, in agreement with the experimentally observed trend of the rate constants and the σ_{rad} values (Table 1).

Solvent effects

A decrease in the decarbonylation rate constant in polar solvents has been noted previously.[4,9,13] Our data confirm this solvent effect not only for the parent compound, but also for all substituted derivatives (with a factor of ~3 difference between *n*-hexane and acetonitrile, Table 1). In the detailed study on the solvent effect for the parent phenacetyl radical,[13] it was concluded that this reduction in the rate constant arises from a dipole moment effect, i.e. the reacting phenacetyl radical is more polar (μ = 2.54 D) and stabilized to a higher degree by solvent than the essentially non-polar products, the benzyl radical (μ = 0.03 D) and carbon monoxide (μ = 0.05 D).

The calculation of the differences in dipole moments of the substituted phenacetyl versus the benzyl radicals (using the previously employed AM1 method,[30] Table 2) revealed a similar decrease in the dipole moment upon going to most substituted benzyl radicals but, interestingly, an increase was predicted for the *p*-CF_3 case, where the benzyl radical has a larger dipole moment. This contrast is, of course, not surprising, since attached aryl substituents may well counterbalance the dipolar effects of the carbonyl group. Note that the total molecular dipole moment presents a vectorial combination of the individual contributions from the attached aryl groups. The calculated increase in dipole moment upon decarbonylation of the *p*-CF_3 phenacetyl radical (positive $\Delta\mu$ value in Table 2) contrasts the experimentally observed decrease in its reactivity in acetonitrile (Table 1). Hence the rationalization of the observed solvent effect in terms of calculated molecular dipole moment[13] may not be universal.

We suggest tentatively that dipole moment effects are important, but it may be the response of the solvent in the immediate environment to the bond being broken, i.e. charge distributions or local changes in the bond dipoles, which are responsible for the observed solvent effect. This rationalization should apply for all derivatives since the decarbonylation reaction entails an effective charge shift from the carbonyl to the benzyl moiety during reaction (Scheme 3). This is corroborated by the AM1-calculated atomic charges, which predict the carbonyl group (C and O atoms) of the phenacetyl radical to carry a negative partial charge (-0.10 ± 0.01 for all derivatives). This charge must be shifted to the benzyl group in the decarbonylation step.

CONCLUSIONS

The electronic substituent effects on the decarbonylation

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of phenacetyl radicals indicate that both electron-withdrawing and electron-donating *para* substituents accelerate the reaction slightly. The kinetics appears to depend primarily on the ability of the aryl substituent to stabilize the benzyl radical resulting from decarbonylation and to weaken the C—CO bond being broken. This is in accordance with the previously observed Evans–Polanyi relationship.[7] Evidence for a polar effect in this reaction, which had been previously detected for the related deazatization of phenylazomethanes,[26] was not obtained.

Acknowledgements

This work was supported by the Swiss National Science Foundation and the Fonds der Chemischen Industrie.

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