Benzoyl σ-Radicals: the Barrier to Internal Rotation

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Rotational barriers of some *para*-substituted benzoyl radicals have been measured by e.s.r. techniques: the linear correlation between the e.s.r. $\Delta G^\ddagger$ values and the corresponding n.m.r. $\Delta G^\ddagger$ values allows us to estimate the free energy of activation of the unsubstituted benzoyl radical [$\Delta G^\ddagger$ 2.8 ± 0.15 kcal mol^{-1} (11.8 ± 0.6 kJ mol^{-1})].

The rotational barrier around the phenyl–carbonyl bond in benzaldehyde and in its *para*-substituted derivatives has been measured by a dynamic n.m.r. method using a ^{13}C Fourier transform technique.[1—3] However, there have been no comparable studies on the corresponding benzoyl σ-radicals. Krusic and Rettig[4] inferred that, in the benzoyl radical, the rotation of the acyl moiety is hindered by a relatively small barrier, too low to be measured by e.s.r. techniques.

It has been recently proposed that a parallel behaviour exists between the rotational barrier in the acyl radicals and in the parent aldehydes.[5,6] In particular, it has been suggested that when the molecule has a barrier lower than about 9 kcal mol^{-1}† the corresponding acyl radical would have a barrier too low to be determined by e.s.r. On the other hand, when the molecule has a barrier higher than about 10 kcal mol^{-1}, the barrier of the corresponding acyl radical should be sufficiently high to be determined, unless the radical decays at high temperature.

The n.m.r. $\Delta G^\ddagger$ data show that the barrier is related to the resonance contribution of the *p*-substituent: the greater the electron-releasing power of the substituent, the higher the torsional barrier. Accordingly, it is conceivable that acyl radicals containing electron-donating substituents might have rotational barriers higher than that of the unsubstituted benzoyl; the corresponding values might thus be amenable to a precise determination by e.s.r. techniques.

We report here a quantitative study of the hindered rotation in benzoyl radicals (**1**)—(**4**) obtained by photolysis of a cyclopropane solution of *p*-substituted benzaldehydes in the presence of di-t-butyl peroxide. The energy barriers and the

$$\mathrm{Bu^tO{-}OBu^t} \xrightarrow{h\nu} \mathrm{2Bu^tO\cdot}$$

$$p\text{-}\mathrm{XC_6H_4CHO} + \mathrm{Bu^tO\cdot} \rightarrow p\text{-}\mathrm{XC_6H_4\dot{C}O} + \mathrm{Bu^tOH}$$

(**1**) X = H
(**2**) X = Me
(**3**) X = OMe
(**4**) X = $\mathrm{NMe_2}$

hyperfine splitting (h.f.s.) constants obtained at different temperatures are collected in Table 1.

The e.s.r. spectra of all the examined *p*-substituted benzoyl radicals display alternating line-width effects, which are temperature dependent. This phenomenon is the same as has been reported[4] for the benzoyl radical, and depends upon the restricted rotation around the Ar–CO bond.

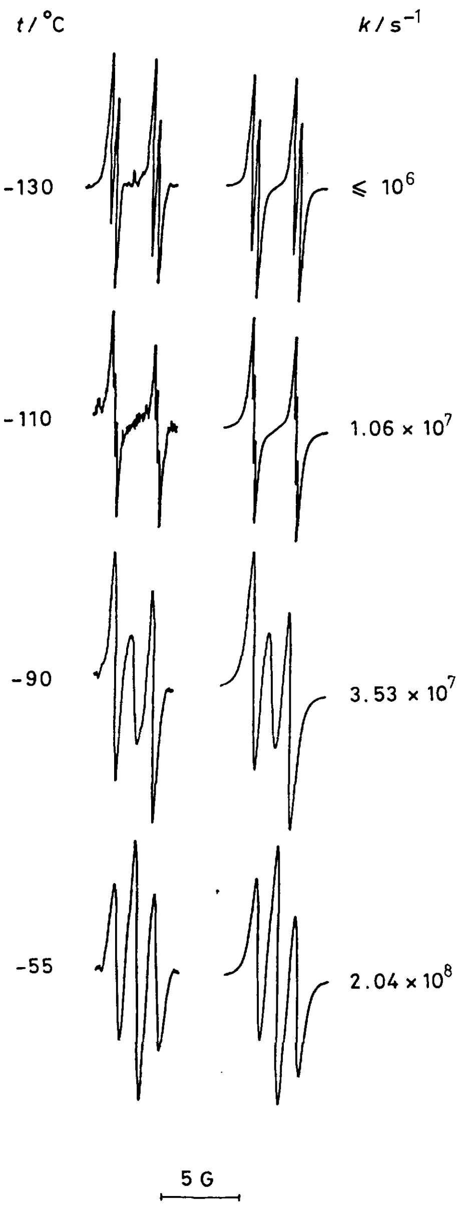

Figure 1. Experimental spectrum of *p*-methoxybenzoyl radical (**3**) at selected temperatures (left) with the corresponding computer simulation (right). Above *ca.* −90 °C the *ortho* triplet is unresolved.

In the case of *p*-methoxybenzoyl radical (**3**), the rotation about the acyl fragment is rapid on the e.s.r. time scale above *ca.* −50 °C, and a time-averaged spectrum, consisting of a 1 : 2 : 1 triplet splitting (a_{2H} 1.15 G)‡ due to the *meta*-protons, is observed. At −100 °C two separated lines with a_H 2.3 G are detected: at this temperature there is therefore a hyperfine splitting of only one of the two *m*-protons, the splitting of the other being almost negligible. Such an interpretation is supported by the fact that the triplet has a splitting (a_{2H} 1.15 G) that is the average of 2.3 G and zero. INDO calculations[4] suggest that the larger coupling (a_H 2.3 G) comes from the *m*-proton adopting a W-relationship with respect to

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† 1 cal = 4.18 J.

‡ 1 G = 10^{-4} T.

Table 1.

Substituent	t/°C	a_H/G (*ortho*)	a_H/G (*meta*)	g	$\Delta G^‡$ e.s.r. kcal mol^{-1}	$\Delta G^‡$ n.m.r.^{b} kcal mol^{-1}
H	−86	0.17 (2H)	1.15 (2H)	2.0006	$2.8^a \pm 0.15$	7.6
Me	−65	—	1.1 (2H)	2.0006	3.3 ± 0.15	8.15
	−140	—	2.2 (1H)			
OMe	−50	—	1.15 (2H)	2.0010	$4.2^c \pm 0.15$	9.0
	−100	0.2 (2H)	2.3 (1H)			
	−130	0.4 (1H)	2.3 (1H)			
NMe_2	−52	—	2.25 (1H)	2.0011	5.7 ± 0.15	10.7
	−100	0.4 (1H)	2.2 (1H)			

^{a} See text. ^{b} Ref. 3 ($CHCl_2F–CCl_2F_2$ as solvent). ^{c} $\Delta H^‡$ 4.6 ± 0.3 kcal mol^{-1}, $\Delta S^‡$ 2.6 ± 2.1 cal mol^{-1} K^{-1}.

the singly occupied σ-orbital, in accord with Russell's empirical formulation for long-range interactions.[7] Spectra obtained at higher resolution, at the same temperature (−100 °C), show each line as a 1 : 2 : 1 triplet (a_{2H} 0.2 G) due to the pair of equivalent *ortho*-protons. This observation implies an averaging process which is still fast compared with the hyperfine frequency difference of these hydrogens. This averaging becomes incomplete, however, at temperatures below −100 °C; we could reach a temperature sufficiently low to allow the observation of two inequivalent *o*-protons. As in the case of the *m*-protons, the splitting of one of the two *o*-protons (a_H 0.4 G) is twice as large as that observed at higher temperatures (*i.e.* the triplet splitting of 0.2 G at −100 °C).

Computer simulation of the spectra at different rates of exchange is shown in Figure 1.

The presence of the *p*-methoxy substituent makes the rotational barrier around the C–CO bond higher than that for the benzoyl radical, in agreement with our prediction.

In the case of the *p*-methyl radical (**2**), owing to the quite low barrier, $\Delta G^‡$ was determined by following the shape of the lines corresponding to the *m*-hydrogen splittings. On the other hand, in the case of the *p*-dimethylamino radical (**4**), owing to the quite high barrier, $\Delta G^‡$ was determined by following the shape of the lines corresponding to the *o*-hydrogen splittings.

From the first order rate constants, obtained by fitting the experimental to the computed spectra, an average value for the energy barriers was determined.

The torsional barrier in the benzoyl radicals depends on the electron-releasing power of the group in *p*-position as observed in the parent molecules. The e.s.r. $\Delta G^‡$ values are about 5 kcal mol^{-1} lower than the n.m.r. $\Delta G^‡$ values.§

For radical (**3**) the $\Delta H^‡$ and $\Delta S^‡$ were also determined (Table 1). Since the activation entropy is negligible within the errors, the $\Delta G^‡$ value for this radical, and most likely for the other radicals examined, can be taken as a reliable measure of the rotational barrier.

We have found a linear correlation between the free energies of activation in the *p*-substituted benzoyl radicals and those in the corresponding benzaldehydes. From this correlation the torsional barrier of benzoyl radical (**1**), too low to be experimentally determined, could be estimated ($\Delta G^‡$ 2.8 ± 0.15 kcal mol^{-1}).

The same $\Delta G^‡$ value was also obtained when the free energies of activation of the examined radicals were plotted against σ_p^+ constants.[8] As previously reported,[3,9] the $\Delta G^‡$ values of torsional processes can be better correlated with σ_p^+ than with the original Hammett constants.

It is noteworthy that the h.f.s. constants observed for the benzoyl radical in the fast exchange region[4,10] seem to be unaffected by the introduction of different electron-donating groups in *p*-position. We can thus reasonably assume that the coupling constants of the benzoyl radical (**1**) in the slow exchange region are approximately equal to those of the *p*-substituted radicals. By using the a_H values found for (**2**)—(**4**), computer simulation of the benzoyl radical spectra gives the kinetic constants for the torsional process. The free energy of activation determined in this way ($\Delta G^‡$ 2.75 ± 0.15 kcal mol^{-1}) turns out to be equal to that previously extrapolated.

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References

1 T. Drakenberg, R. Jost, and J. Sommer, *J. Chem. Soc., Chem. Commun.*, 1974, 1011.
2 L. Lunazzi, D. Macciantelli, and A. C. Boicelli, *Tetrahedron Lett.*, 1975, 1205.
3 T. Drakenberg and J. Sommer, *J. Chem. Soc., Perkin Trans. 2*, 1980, 363.
4 P. J. Krusic and T. S. Rettig, *J. Am. Chem. Soc.*, 1970, **92**, 722.
5 C. Chatgilialoglu, L. Lunazzi, D. Macciantelli, and G. Placucci, *J. Am. Chem. Soc.*, 1984, **106**, 5252.
6 L. Lunazzi, G. Placucci, C. Chatgilialoglu, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1984, 819.
7 G. A. Russell, 'Radical Ions,' eds. L. Kevan and E. T. Kaiser, Interscience Publishers, New York, 1968, p. 87.
8 O. Exner, 'Advances in Linear Free Energy Relationship,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1972, p. 32.
9 S. S. Kim and S. C. Sohn, *Tetrahedron Lett.*, 1982, **23**, 3703.
10 H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575.

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§ The lower barrier in the benzoyl radicals may be attributed to the relative stability of the bisected form, involved in the equilibrium conformation of the coplanar structure, where the loss of resonance interaction with the carbonyl group is partially compensated by the greater delocalization of the unpaired electron, ref. 4.