6 H), 6.90 (s, 6 H), and 8.35 (s, 15 H)). No significant line broadening was observed up to 167° though there appeared to be a slight high-field shift of the central carbomethoxy resonance again at this temperature. A rearrangement with $k \leq 3$ sec$^{-1}$ could have been detected. The $\Delta F^{\ddagger}$ for the iridium complex is therefore at least 25 kcal mol$^{-1}$, and this rearrangement occurs much less readily here.[12]

It is intriguing to speculate that a process involving formation of an intermediate corresponding to **1** ($R' =$ Me) but with Cl and $\pi$-bonded hexamethyl(Dewar benzene) (HMDB) in place of $C_5Me_5$, may be involved in the $[(HMDB)RhCl]_2$-catalyzed isomerization of HMDB to hexamethylbenzene recently reported by Volger and Hogeveen.[15]

**Acknowledgment.** We thank the National Research Council of Canada and the Petroleum Research Fund administered by the American Chemical Society (Grant 1796-Al) for support of this work.

(12) We have also compared the rates of rotation of ethylene about the ethylene–metal axis for $C_5Me_5M(C_2H_4)_2$ and find this to be slower for M = Ir than for M = Rh. This appears to be a general phenomenon for 4d and 5d metals; Cotton, *et al.*, have shown that fluxional behavior is slower, and $\Delta H$ higher, for $C_8H_4Me_4W(CO)_3$ than for $C_8H_4Me_4Mo(CO)_3$,[13] and Bruce, *et al.*, have observed the same for $C_8H_8Os(CO)_3$ and $C_8H_8Ru(CO)_3$.[14]

(13) F. A. Cotton, J. W. Faller, and A. Musco, *J. Amer. Chem. Soc.*, **90**, 1438 (1968).

(14) M. I. Bruce, M. Cooke, and M. Green, *Angew. Chem. Intern. Ed. Engl.*, 7, 639 (1968).

(15) H. C. Volger and H. Hogeveen, *Rec. Trav. Chim. Pays-Bas*, **86**, 831 (1967).

(16) Fellow of the Alfred P. Sloan Foundation and author to whom any correspondence should be directed.

**J. W. Kang, R. F. Childs, P. M. Maitlis**[16]
*Chemistry Department, McMaster University*
*Hamilton, Ontario, Canada*

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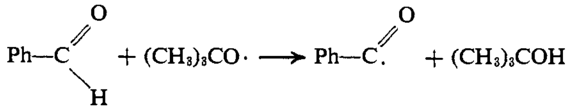
## Electron Spin Resonance Study of Benzoyl $\sigma$ Radicals in Solution

*Sir:*

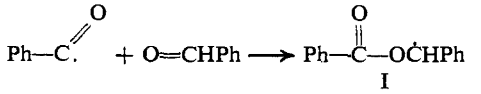
In sharp contrast to the voluminous literature concerned with the electron spin resonance (esr) of $\pi$ radicals, there exist very few experimental[1] or theoretical[2] studies on organic $\sigma$ radicals. In such radicals the unpaired electron is mainly localized in an orbital with nonvanishing amplitude at the nucleus of the radical center. Most of these investigations, moreover, were carried out in rigid matrices, except for the vinyl and methylvinyl radicals[3] and a few aliphatic acyl radicals derived from formamide and substituted formamides[4] by abstraction of the aldehyde hydrogen atom. In this report we present an esr study of a number of benzoyl radicals in solution.[5] The esr spectra of these radicals permit the study of the delocalization of unpaired spin density from the $\sigma$ system of the acyl moiety into the adjacent phenyl substituent.

Photolysis of a stationary cyclopropane solution of benzaldehyde in the presence of di-*t*-butyl peroxide[6] gives an esr spectrum consisting of a 1:2:1 triplet of 1.16-G separation ($g$ value = 2.0014) over a wide temperature range. An extremely weak identical spectrum was obtained in the absence of the peroxide.[7] We assign the spectrum (*vide infra*) to the benzoyl radical, formed by abstraction of the aldehyde hydrogen atom by *t*-butoxy radical (eq 1). No esr evidence was obtained for the $\alpha$-hydroxybenzyl radical which would be formed by photoreduction of benzaldehyde[8,9] (eq 2) or for the ester radical I, which was postulated as an intermediate in the thermal decomposition of di-*t*-butyl peroxide in the presence of benzaldehyde.[10]



$$\mathrm{PhCHO} + (\mathrm{CH_3})_3\mathrm{CO}\cdot \longrightarrow \mathrm{Ph{-}\dot{C}{=}O} + (\mathrm{CH_3})_3\mathrm{COH} \qquad (1)$$

$$\mathrm{PhCHO}^3(\mathrm{n},\pi^*) + \mathrm{RH} \longrightarrow \mathrm{Ph\dot{C}HOH} + \dot{\mathrm{R}} \qquad (2)$$



$$\mathrm{Ph{-}\dot{C}{=}O} + \mathrm{O{=}CHPh} \longrightarrow \mathrm{Ph{-}C({=}O){-}O\dot{C}HPh} \qquad (3)$$

I

Under the same conditions, benzaldehyde-2,4,6-$d_3$ also gave the same triplet (Figure 1), but with narrower line widths (Table I). Since both benzaldehyde-3,5-$d_2$ and benzaldehyde-2,3,4,5,6-$d_5$ show collapse of the triplet into a single unresolved line, which is of greater line width than the lines of either the undeuterated or the 2,4,6-$d_3$ species, we conclude that *the major proton hyperfine splitting (1.16 G) is due to the meta hydrogens*

**Table I.** Hyperfine Coupling Constants of Benzoyl Radicals[a]

| Starting compound | Type of spectrum | Temp, °C | Coupling Constants, G $a_{mH}$ | $a_{^{13}C}$[c] | $\Delta H$,[b] G |
|---|---|---|---|---|---|
| Benzaldehyde | Triplet | −86 | 1.16 | 128.2 | 0.35 |
| Benzaldehyde-2,4,6-$d_3$ | Triplet | −89 | 1.17 | | 0.21 |
| Benzaldehyde-3,5-$d_2$ | Singlet | −103 | | | 0.65 |
| Benzaldehyde-2,3,4,5,6-$d_5$ | Singlet | −83 | | | 0.63 |

[a] From photolysis of cyclopropane solutions of substituted benzaldehydes in the presence of di-*t*-butyl peroxide (1/1/1, v/v/v). [b] Peak-to-peak line width. [c] From benzaldehyde-7-$^{13}$C (50 atom %).

(1) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962); **43**, 462 (1965); E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964); **44**, 4626 (1966); J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965); *Proc. Roy. Soc.* (London), **A293**, 246 (1966); J. E. Bennett, B. Mile, and B. Ward, *Chem. Commun.*, 13 (1969); H. J. Bower, J. A. McRae, and M. C. R. Symons, *ibid.*, 542 (1967); I. Miyogawa and W. Gordy, *J. Chem. Phys.*, **30**, 1590 (1959); M. C. R. Symons, *J. Chem. Soc.*, 1189 (1963); Y. Kurita, *J. Chem. Soc. Jap.*, **86**, 581 (1965); H. Hayashi, K. Itoh, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **40**, 284 (1967); R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, 71, 14 (1967); N. Cyr and W. C. Lin, *J. Chem. Phys.*, **50**, 3701 (1969).

(2) F. J. Adrian and M. Karplus, *ibid.*, 41, 56 (1964); W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965); G. A. Petersson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966); N. M. Atherton and A. Hinchliffe, *Mol. Phys.*, **12**, 349 (1967); R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, 88, 1071 (1966); R. S. Drago and H. Petersen, Jr., *ibid.*, **89**, 5774 (1967); J. A. Pople, D. L. Beveridge, and P. A. Dobosh; *ibid.*, **90**, 4201 (1968).

(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967).

(4) R. Livingston and H. Zeldes, *J. Chem. Phys.*, 47, 4173 (1967); T. Yonezawa, I. Noda, and T. Kawamura, *Bull. Chem. Soc. Jap.*, **41**, 766 (1968); **42**, 650 (1969).

(5) Benzoyl radicals have been recently studied in solid matrices (U. Schmidt, K. Kabitzke, and K. Markau, *Monatsh. Chem.*, **97**, 1000 (1966)). A single, broad line was reported.

(6) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968).

(7) Benzoyl radicals formed under these conditions were probably formed by adventitious peroxides.

(8) R. Wilson, *J. Chem. Soc.*, *B*, 84 (1968).

(9) Previous studies (*cf.* ref 6) have shown that cyclopropane is a poor hydrogen donor. It has been, therefore, widely used as "inert" solvent in these experiments.

(10) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 70, 3258 (1948).

**Table II.** Hyperfine Coupling Constants of Fluorinated Benzoyl Radicals[a]

| Starting compound | Type of spectrum | Temp, °C | Hyperfine coupling constants, G $a_{m\mathrm{H}}$ | $a_{o\mathrm{F}}$ | $a_{m\mathrm{F}}$ | $a_{p\mathrm{F}}$ |
|---|---|---|---|---|---|---|
| *o*-Fluorobenzaldehyde | Two triplets | −88 | 0.85 | 1.46 | | |
| *m*-Fluorobenzaldehyde | Two doublets | −85 | 1.25 | | 3.43 | |
| *p*-Fluorobenzaldehyde | Three doublets | −50 | 1.14 | | | 0.3[b] |
| Perfluorobenzaldehyde | Three triplets | −122 | | 0.71 | 3.17 | [c] |

[a] From photolysis of cyclopropane solutions of substituted benzaldehydes in the presence of di-*t*-butyl peroxide (1/1/1, v/v/v). [b] Accurate to ±0.1 G because of incomplete resolution. [c] Unresolved.

rendered equivalent by a fast averaging process (*vide infra*). Moreover, both the unusually small *g* value[11] and the very large magnitude (128.2 G) for the $^{13}$C splitting of the radical derived from benzaldehyde-7-$^{13}$C (50% enriched sample) confirm the "non-π" nature of the benzoyl radical.[12]

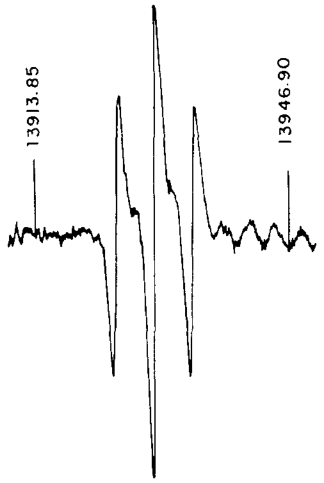


Figure 1. Esr spectrum of benzoyl radical obtained by abstraction of the aldehyde hydrogen from benzaldehyde-2,4,6-$d_3$ in cyclopropane solution at −89°. The proton nmr field markers are in kHz.

The aldehyde hydrogen atom was also abstracted under the same conditions from a series of fluorobenzaldehydes (Table II). The spectra obtained from *o*-fluoro-, *m*-fluoro-, and *p*-fluorobenzaldehyde are shown in Figure 2. The assignments, based on internal consistency, associate the largest interaction with the *meta* substituent followed by the *ortho* and *para* substituents, respectively. This is in contrast with the more familiar *para* > *ortho* > *meta* trend observed with benzylic π radicals.[13]

The observation that only the *meta* hydrogens exhibit appreciable unpaired spin density is unprecedented. The results of INDO molecular orbital calculations[14] for two static and two dynamic models of the benzoyl radical are presented in Table III. The large observed 7-$^{13}$C coupling constant, indicative of substantial s character of the lone electron orbital, clearly precludes a linear "π" structure for the benzoyl radical. The prediction of a relatively large *meta* coupling constant for the planar model is in gratifying agreement with the experiment. The pronounced *trans* effect in the *meta* position[15] as well as the positive sign of the coupling constant of the *trans meta* hydrogen are indica-

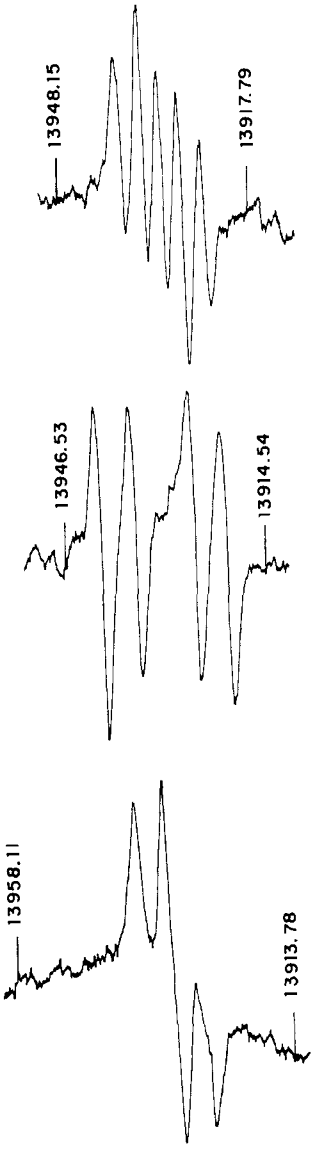


Figure 2. Esr spectra of *o*-fluorobenzoyl, *m*-fluorobenzoyl, and *p*-fluorobenzoyl radicals (top to bottom) in cyclopropane solution.

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(11) *g* values less than the spin-only value of 2.00232 are rare for organic free radicals in solutions (*cf.* ref 3 and 4).

(12) The large $^{13}$C splittings in aliphatic σ radicals have been discussed: E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 44, 4626 (1966); R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967).

(13) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 4857 (1964); A. Carrington and I. C. P. Smith, *Mol. Phys.*, 9, 137 (1965); H. Fischer, *Z. Naturforsch.*, *A*, 20, 488 (1965); J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 49, 4725 (1968); *cf.* Krusic and Kochi.[6]

(14) (a) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968); (b) we obtained a copy of this program from the Quantum Chemistry Program Exchange, Indiana University.

(15) The *trans* effect in the *meta* position is in accord with Russell's empirical *W*-plan formulation for long-range interactions: G. A. Russell, "Radical Ions," L. Kevan and E. T. Kaiser, Ed., Interscience Publishers, New York, N. Y., 1968, p 87 ff.

**Table III.** INDO Hyperfine Coupling Constants (G) for the Benzoyl Radical[a]

| | Planar[b] *cis* | Planar[b] *trans* | Linear[c] | Free rotation[d] | High barrier[e] | Experimental[f] |
|---|---|---|---|---|---|---|
| $a_{\mathrm{H}(ortho)}$ | 1.21 | −0.10 | −5.49 | 0.30 | 0.56 | <0.1 |
| $a_{\mathrm{H}(meta)}$ | −0.13 | 2.72 | 3.08 | 1.36 | 1.30 | 1.16 |
| $a_{\mathrm{H}(para)}$ | 0.02 | 0.02 | −4.92 | −0.46 | 0.02 | <0.1 |
| $a_{^{13}\mathrm{C}}$[g] | 129.72 | 129.72 | 21.88 | 120.17 | 129.72 | 128.2 |

[a] The structure used for the calculations assumes a regular hexagon for the phenyl group with $d$(C,C) = 1.39, $d$(C,H) = 1.08, $d(C_1,C_7)$ = 1.40, $d(C_7,O)$ = 1.21 Å, and $\alpha(C_1,C_7,O)$ = 120°. [b] The nomenclature *cis* and *trans* refers to the unpaired electron mainly localized in an $sp^2$ hybrid orbital on $C_7$. [c] Same assumed structural parameters except for $\alpha(C_1,C_7,O)$ = 180°. [d] Isotropic average of the coupling constants calculated over a rotation of 180° about the $C_1$–$C_7$ bond in increments of 10°. [e] Average of the coupling constants for the *cis* and *trans* hydrogens. [f] Absolute values. [g] Coupling constant for $C_7$.

tive of delocalization of unpaired spin density directly into the $\sigma$ system of the phenyl substituent.

Unfortunately, one cannot distinguish, on the basis of the results of Table III alone, between the two dynamic models in question, *i.e.*, free rotation of the carbonyl group about the $C_1$–$C_7$ bond or a sizable twofold barrier to rotation with a coplanar conformation at the minimum. The observation of a 1:2:1 triplet splitting due to the *meta* protons implies an averaging process which is fast compared with the hyperfine frequency difference of the *meta* protons. This averaging becomes incomplete, however, at temperatures below −120° as evidenced by a pronounced broadening[16] of the central line of the triplet. We infer that the rotation of the acyl moiety is hindered by a relatively small barrier and that the equilibrium conformation corresponds to the coplanar structure.[17,18] A quantitative treatment of the hindered rotation in the benzoyl radical is in progress.

**Acknowledgments.** We thank Dr. Paul Meakin for helpful discussion, and Mr. K. Eaby for assistance with the experimental work.

(16) Line-width effects in esr spectroscopy have been reviewed recently: D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1965); G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967); A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

(17) The equilibrium conformation with the $C_1C_7O$ plane bisecting the phenyl ring, with *equivalent ortho* and *meta* hydrogens, cannot cause the observed line broadening.

(18) This relatively low barrier is surprising. Infrared[19] and nmr[20] studies indicate a barrier for benzaldehyde of the order of 7 kcal/mol. In two related radicals, $\alpha$-hydroxybenzyl[8] and the benzaldehyde radical anion,[21] the barrier must also be very high since these radicals possess distinct *ortho* and *meta* hydrogens. The lower barrier in the benzoyl radical may be attributed to the relative stability of the bisected form where the loss of resonance interaction with the carbonyl group is partially compensated by the greater delocalization of the unpaired electron.

(19) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).

(20) F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, **86**, 119 (1964).

(21) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

**P. J. Krusic, T. A. Rettig**

*Contribution No. 1625, Central Research Department*
*E. I. du Pont de Nemours and Co., Experimental Station*
*Wilmington, Delaware 19898*

*Received November 22, 1969*

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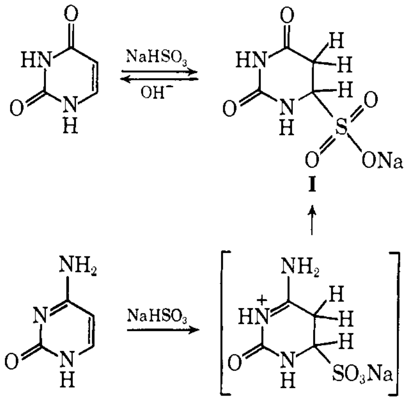
## The Addition of Sodium Bisulfite to Uracil and to Cytosine

*Sir:*

Our recent discovery of an oxygen-mediated reaction between 4-thiouridine and sodium sulfite,[1] which brings about the formation of uridine-4-sulfonate,[2] has led us to investigate the effect of sodium sulfite on other nucleoside bases.

Uracil was found to react with $NaHSO_3$ at pH ~6. A typical reaction procedure is as follows. A suspension of uracil (224 mg, 2 mmol) in water (10 ml) was heated at 66°. Into it was added a mixture of $NaHSO_3$ (12 mmol) and $Na_2SO_3$ (3 mmol). A complete solution resulted within 1 min and precipitation of a product started in 3 min. After 30 min of heating, when the reaction was complete as judged by the loss of absorption at 260 mμ of the reaction solution ($A_{260\ \mathrm{m}\mu}$ value of the supernatant solution was found to be less than 5% of the original value), the reaction mixture was chilled in ice and the prism crystals of the product (I) were collected by filtration (yield, 375 mg). No other product than I was detected in the reaction mixture by paper chromatographic analysis.

**Chart I**



When I was paper chromatographed (solvent: *t*-amyl alcohol–formic acid–$H_2O$, 3:2:1, v/v), no uv-absorbing spot was detectable on the chromatogram. After 0.1 *N* NaOH solution was sprayed on the chromatogram, however, a strongly uv-absorbing spot with an $R_f$ value of 0.58 became detectable ($R_f$ of uracil was 0.70). Uv absorption spectra of this alkali-treated I in acid and in alkali were identical with those of uracil. Paper chromatography of the alkali-treated I gave a single spot whose $R_f$ value was the same as that of uracil. This fact has indicated that I readily regenerates uracil on treatment with alkali.

Interestingly, cytosine gave I upon treatment with sodium sulfite at pH about 6. Thus, when a solution of cytosine (2 mmol) in water (5 ml) was treated with a mixture of $NaHSO_3$ (12 mmol) and $Na_2SO_3$ (3 mmol) at 80° for 30 min, a crystalline product (340 mg) was obtained as an insoluble precipitate. Identity of this product with I was established by paper chromatography, paper electrophoresis (see below), uv and ir spectra, and the regeneration of uracil on treatment with alkali.

The following evidences have established the structure of I to be sodium 5,6-dihydrouracil-6-sulfonate.

(1) H. Hayatsu, *J. Amer. Chem. Soc.*, **91**, 5693 (1969).

(2) H. Hayatsu and M. Yano, *Tetrahedron Lett.*, 755 (1969).