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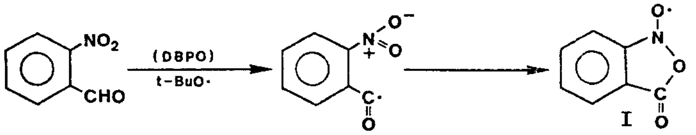
AN ESR AND ENDOR STUDY OF INTRAMOLECULAR AND INTERMOLECULAR ADDITION REACTIONS OF BENZOYL AND SUBSTITUTED BENZOYL RADICALS TO NITROAROMATIC COMPOUNDS. A TWO-STEP OXYGEN ATOM ABSTRACTION REACTION.

Edward G. Janzen and Uwe M. Oehler
Department of Chemistry
Guelph-Waterloo Centre for Graduate Work in Chemistry
University of Guelph
Guelph, Ontario, N1G 2W1

Summary: Persistent cyclic acyloxy aminoxyl radicals can be obtained by intramolecular trapping of benzoyl radicals by adjacent aromatic nitro groups whereas analogous intermolecular acyloxy adducts decay by N-O cleavage to give C-nitroso compounds and ultimately acyl aminoxyls.

Iwamura and Inamoto[1] were searching for an oxygen abstraction reaction in the thermal decomposition of bis-isobutyronitrile in the presense of nitrones.[2] Instead 2-cyanopropyl radicals add to the carbon atom of the nitronyl function yielding persistent aminoxyls.[1,3] Our work demonstrates that benzoyl radicals are capable of abstracting oxygen atoms from the nitro group of nitroaromatic compounds by a two-step radical addition-cleavage mechanism confirming that such reactions are possible for suitable radicals and oxygen atom sources.

Thus when 0.02M di-tert-butylperoxalate (DBPO) is mixed with 0.3M o-nitrobenzaldehyde in benzene at room temperature an esr spectrum (Figure 1) typical of an ortho-substituted aryl aminoxyl radical is obtained: $a_N = 13.75$; $a_p^H = 3.01$; $a_o^H = 2.82$ (1H); $a_m^H = 0.95$ (2H) G. The hyperfine splitting constants (hfsc's) and spectrum are the same as reported by Aurich[4] for a cyclic acyloxy aminoxyl, I. The reaction route suggested involves intramolecular addition of the o-nitrobenzoyl radical to an oxygen atom of the neighbouring nitro group by analogy to similar intramolecular trapping reactions of carbon-centered radicals to ortho-substituted nitro groups[5,6]:



To verify that the spectrum assigned to I is not due to an intermolecular addition product with a small aldehydic H-hfsc the ENDOR spectrum was obtained.

Approximately 0.02M DBPO was added to 0.1M o-nitrobenzaldehyde in room temperature benzene well degassed with N_2. The ESR spectrum of I developes over a period of an hour but is still strong after one day. A small high purity Amersil quartz flat cell[7] suitable for variable temperature ESR work was used. An IBM-Bruker 200D-SRC spectrometer equipped with a 300 Watt RF

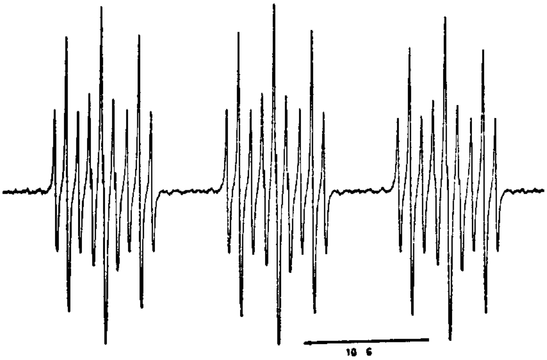


Figure 1

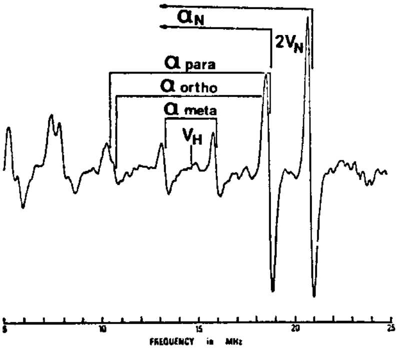


Figure 2

Amplifier and the Bruker Data System[8] was employed. The RF frequency was modulated at 12.5 kHz producing a 1st derivative presentation of the spectrum.

Figure 2 shows the ENDOR spectrum of I on a frequency scale. Room temperature (or slightly above) allowed the best detection of both the proton and the N-14 ENDOR lines in this radical. Typically 10-25 scans were accumulated for good spectra. Six lines are resolved in the 10-25 MHz region (the "noise" below 8 MHz should be ignored[9]). Three doublets are symmetrically placed about the "free" proton Larmor frequency (14.5 MHz at 3400 gauss) due to the meta, ortho and para protons of I (w.r.t. the aminoxyl function). The separations are 26.8, 7.74 and 8.38 MHz (0.96, 2.76 and 2.99 G respectively). The N-14 ENDOR lines are also symmetrically spaced about the free N-14 Larmor frequency (1.06 MHz at 3400 gauss) although the low frequency line is "reflected back" from the origin (0 MHz).[10] The nitrogen hfsc is calculated as follows:

$\frac{1}{2} a_N - \nu_N$ = position of low frequency line; a_N = 39.36 MHz (14.06 G)

$\frac{1}{2} a_N + \nu_N$ = position of high frequency line; a_N = 39.46 MHz (14.09 G)

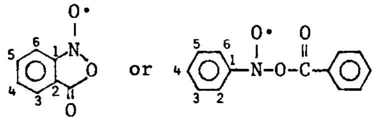
Since no signal at or near ν_H is found this result proves that no small proton hyperfine splitting is concealed in the line-width of the ESR spectrum of I[14]. The assignment of I is thus confirmed.

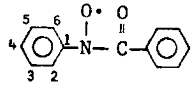
The ready availability of certain methoxynitrobenzaldehydes and dinitrobenzaldehydes prompted ESR experiments with these compounds as well. Thus 3-methoxy-2-nitrobenzaldehyde and 4,5-dimethoxy-2-nitrobenzaldehyde (6-veratraldehyde) gave clean spectra consistent with the structure of I but 2,4- and 2,6-dinitrobenzaldehyde gave ESR spectra due to mixtures. One component of the spectrum from 2,6-dinitrobenzaldehyde could be analyzed and assigned to the 2-nitro derivative of I (see Table I for ESR parameters).

Benzoyl radicals also add to nitrobenzene and substituted nitrobenzenes to produce the previously unreported non-cyclic acyloxy aminoxyl radicals but only in the cases of 1,4-dinitro and 1,3,5-trinitrobenzene are the initial addition products detected at room temperature. Thus

Table I

HYPERFINE SPLITTING CONSTANTS FOR ACYLOXY AND BENZOYL AMINOXYL RADICALS[a]

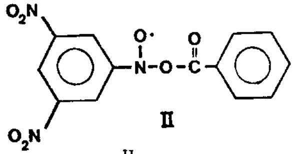




Source	a_N	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H	a_N	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H
2-nitrobenzaldehyde	13.75	-	0.95	3.01	0.95	2.82	-	-	-	-	-	-
3-methoxy-2-nitrobenzaldehyde	14.08	-	0.68	3.09	0.68	0.29	-	-	-	-	-	-
4,5-dimethoxy-2-nitrobenzaldehyde	13.78	-	0.47	0.37	0.10	2.18	-	-	-	-	-	-
2,6-dinitrobenzaldehyde	12.42	-	-	2.76	0.89	2 56	-	-	-	-	-	-
1,3,5-trinitrobenzene	14.48	2.85	-	2.85	-	2.85	7.16	1.59	-	1.59	-	1.59
1,4-dinitrobenzene	13.93	2.85	1.02	0.70[b]	1.02	2.85	7.21	1.63	0.69	0.37[b]	0.69	1.63
3,5-bis-trifluoromethylnitrobenzene	-	-	-	-	-	-	7.2	1.6	0.5[c]	1.6	0.5[c]	1.6
1,3-dinitrobenzene	-	-	-	-	-	-	7.28	1.55	0.65	1.55	-	1.55
1,2-dinitrobenzene	-	-	-	-	-	-	7.79	0.23[b]	0.45	1.03	0.82	0.82
nitrobenzene	-	-	-	-	-	-	7.45	1.54	0.64	1.63	0.64	1.54
3-nitrobenzaldehyde	-	-	-	-	-	-	6.97	1.39	-	1.52	0.65	1.39

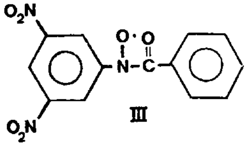
(a) in gauss at room temperature in benzene
(b) nitrogen hyperfine splitting constant
(c) fluorine hyperfine splitting constant

when 0.02M DBPO is reacted with excess benzaldehyde in benzene containing 1,3,5-trinitrobenzene initially a spectrum with a 14.5 G triplet predominates. However another spectrum with a 7.2 G triplet rapidly intensifies and becomes the major final spectrum. These spectra are assigned to the acyloxy and acyl aminoxyl radicals respectively:



II

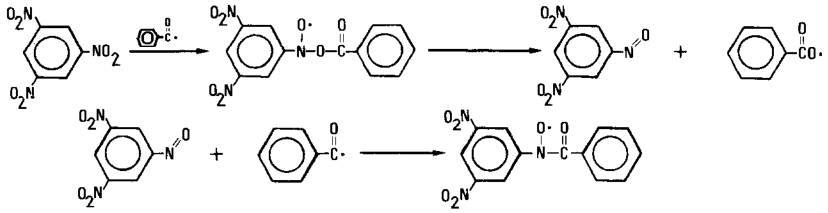
$a_N = 14.48$, $a_{o,p}^H = 2.85$ (3H) G



III

$a_N = 7.16$, $a_{o,p}^H = 1.59$ (3H) G

In the case of nitrobenzene[17], 1,2- and 1,3-dinitrobenzene and 3,5-trifluoromethylnitrobenzene the only spectrum observed is due to the acyl aminoxyl radical. Thus decomposition of II probably produces nitrosobenzene which in turn traps benzoyl radicals (see Table I).



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2. Private communication from Dr. M. Iwamura.
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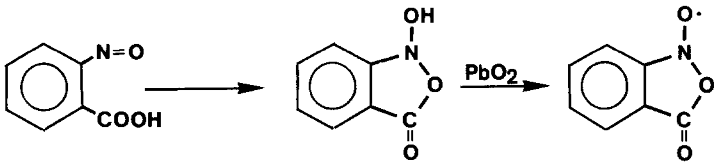

$a_N = 13.6$ G

$a_p^H = 3.0$ G

$a_o^H = 2.8$ G

$a_m^H = 0.95$ G

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6. A.L.J. Beckwith and M.D. Lawton, J. Chem. Soc., Perkin II, 2134 (1973).
7. Window size: 47 mm x 3.5 mm x 5.0 mm; total length 170 mm; plate thickness 1 mm, flat cell volume 0.073 ml; available from IBM Instruments Inc.
8. We are grateful to IBM Instruments Inc. San Jose, Calif. for use of their facilities and equipment.
9. A number of broad peaks of various shapes and sizes were seen in the 0-10 MHz region for various aminoxyls studied; this effect has been attributed to an instrumental cause (private communication with Dr. D. Schmalbein, Bruker, Karlsruhe, W. Germany).
10. The N-14 ENDOR lines are always separated by 2 ν_N for cases where $a_N > 2\nu_N$. See [11,12,13]
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14. Compare for example the ENDOR spectra of bis(p-methoxylphenyl) aminoxyl[15] and the Banfield-Kenyon radical.[16]
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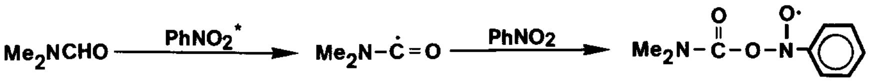
17. A spectrum obtained in the photolysis of nitrobenzene in DMF was previously tentatively assigned to an analog of II:[18]



$a_N = 15.5$, $a_{o,p}^H = 3.0$, $a_m^H = 1.0$ G

18. S.K. Wong and J.K.S. Wan, Can. J. Chem., 51, 753 (1973).

Acknowledgement

The first detection of I was by C.C. Lai as a result of an experiment suggested by E.R. Davis. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada. Grateful acknowledgement is hereby made. We also are thankful to IBM Instruments Inc. for use of their equipment and technical help from Dr. D.D. Thomas and Mr. D.P. Chrisman at IBM Instruments Inc.

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