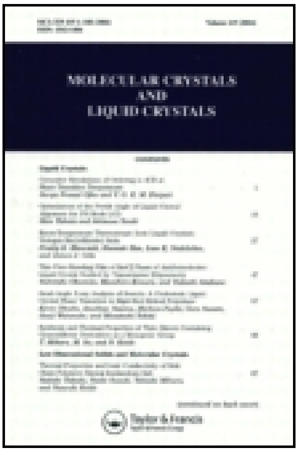

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ESR STUDY ON DIRADICALS GENERATED BY ONE-ELECTRON OXIDATION OF STABLE ORGANIC RADICALS

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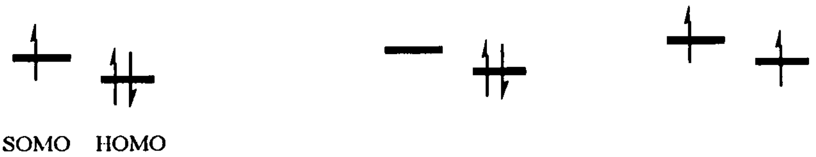
Abstract The electronic structure of cationic species generated by γ-radiolysis of stable organic radicals such as substituted iminoxyls, galvinoxyls, and nitronyl nitroxides, was studied in $CFCl_3$ matrix at 77 K. In most cases, the ESR signals of the radicals were decreased by the one-electron oxidation but the spectra of biradicals were not observed at all. However, *p*-hydroxyphenyl-substituted nitronyl nitroxide exhibited, on radiolysis, ESR signals ranging from 3180 to 3330 G, which was possibly assigned to that of the triplet biradical formed by the oxidation and the following deprotonation.

INTRODUCTION

In order to realize organic ferromagnets, magnetic properties of many charge-transfer salts with a segregated-stack structure have been studied[1] according to the McConnell mechanism.[2] Recently, the difficulty in the ferromagnetic interaction has been suggested for doubly ionized aromatic molecules,[3] but the ferromagnetic coupling between radicals may be derived from the CT interaction if the intermolecular overlap integral between one singly-occupied molecular orbital (SOMO) and a doubly occupied or a vacant orbital of another is lager than the anti-ferromagnetic SOMO-SOMO interaction.[4] However, the charge transfer interaction between radicals generally annihilates their spins since one-electron oxidation or reduction of organic free radicals usually affords ground state singlet cations or anions, respectively. Then, in order to achieve a strong ferromagnetic interaction, it may be desirable that the electron transfer of radicals affords a triplet diradical. Such a radical may also function as a component for ferromagnetic CT-complexes[5] or doped high-spin polymers.[6]

The object of the present work is to prepare such an organic radical to generate a triplet biradical upon electron transfer. Since many stable radicals such as phenoxyls and nitroxides have been prepared by the oxidation of their precursors, the oxidation of radicals may be more promising for the present purpose rather than the corresponding reduction. If a radical has an electronic structure such that the energy level of the highest doubly-occupied MO (HOMO) is close to that of the SOMO, the one-electron removal from the HOMO is expected to generate a triplet cation (eq.1).

$$\mathrm{R}\bullet \xrightarrow{-e} {}^{1}[\mathrm{R}^{+}] \quad \text{or} \quad {}^{3}[\mathrm{R}^{+}] \qquad (1)$$

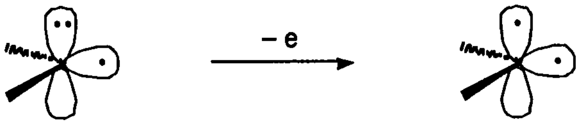


As an another approach, the deprotonation of cations may afford a neutral diradical (eq.2), because organic radical cations are commonly much more acidic than the neutral state.[7] Such a cooperative proton-electron transfer has been known to occur in solid phase.[8]

$$\mathrm{H{-}R}\bullet \xrightarrow{-e,\,-H^{+}} {}^{1}[\mathrm{R}:] \quad \text{or} \quad {}^{3}[\mathrm{R}:] \qquad (2)$$

STRATEGY

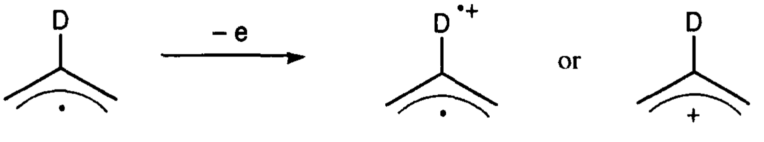
The requirements for the radicals generating the biradicals upon the one-electron oxidation are that the HOMO is in a symmetry different from the corresponding SOMO to avoid the HOMO-SOMO mixing, and that the energy level of the HOMO is to be controlled by substituents and can be as high as that of the SOMO. Then, we could propose two models as the suitable structure. One is a σ-radical with conjugated π-system (**1**), which may afford a σ-π biradical (**2**) similar to carbenes or nitrenes if one electron is removed from the π-orbital.



1 **2**

(3)

Another is an allylic radical **3** in which a strong electron-donating group is substituted on the central atom. The resulting cation may be either trimethylenemethane-type biradical (**4**) or singlet allyl cation (**5**).

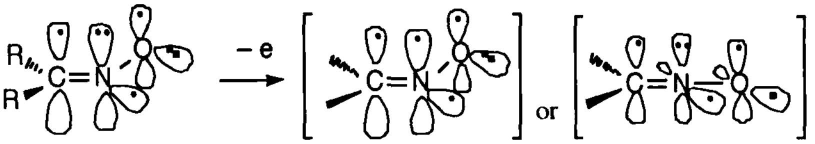


3 4 5 (4)

In order to study the electronic structure of unstable cationic species, the one-electron oxidation of the radicals was carried out by γ-radiolysis in $CFCl_3$ matrix at 77 K. The details of the radiolysis and ESR experiments are identical as described before.[9]

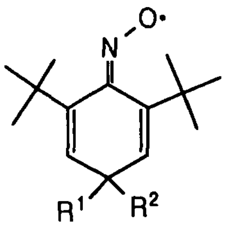
RESULTS

Iminoxyl radicals (**6**, R = t-Bu[10] or 1-adamantyl[11]) are known as an isolable σ-radical. The one-electron oxidation of iminoxyls is to afford α-nitroso carbocations, which are isoelectronic to diazoalkanes. According to the ab initio MP3/4-31G//UHF/4-31G and the semi-empirical AM1-CI (6 electrons in 5 orbitals) calculations for the parent iminoxyl (**6**, R = H), the singlet state is 25.4 and 20.5 kcal/mol, respectively, lower in energy than the triplet. However, the triplet state of $PhCH{=}NO^+$ was calculated by the AM1-CI to be 6.2 kcal/mol lower than the singlet. Thus, the triplet state may be more stable if the π-orbital is conjugated with substituents.



6 *Triplet* *Singlet* (5)

The iminoxyl (**6**, R = t-Bu) was oxidized by the γ-radiolysis in $CFCl_3$ matrix at 77 K. ESR signal of the radical decreased, but spectrum of corresponding biradicals were not observed at all. A bulky iminoxyl, **7** (R^1 = t-Bu, R^2 = i-Pr)[12] was oxidized similarly, resulting in no observation of ESR signals. We prepared new iminoxyls such as **8**, but the radicals were too unstable to be tested by the radiolysis. An attempt for the preparation of stable iminoxyls with electron-donating substituents is under way.



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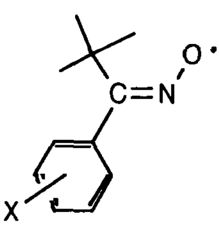

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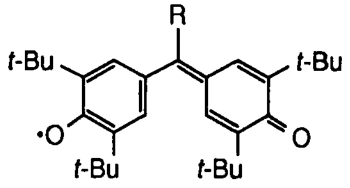

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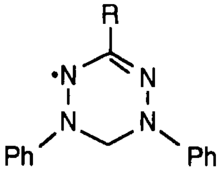

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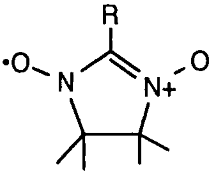

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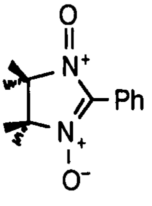
Then, stable allylic-type radicals such as galvinoxyls (**9**),[13] verdazyls (**10**),[14] and nitronyl nitroxides (**11**)[15] with electron-donating substituents on the central atom were examined. The oxidation potentials for 9, 10, and 11 (R = Ph) were +0.09, +0.07, and +0.63 V vs Ag/AgCl, respectively, as determined by cyclic voltammetry in acetonitrile solution at room temperature. The nitronyl nitroxide **11** with a moderate oxidation potential was expected to be employed as a precursor for biradicals, while the potentials of the galvinoxyl and the verdazyl seemed to be too low. However, it have been already known that some cations of nitronyl nitroxides such as **12**[15] and **13**[16] are diamagnetic species in solution.



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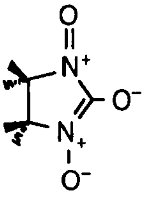

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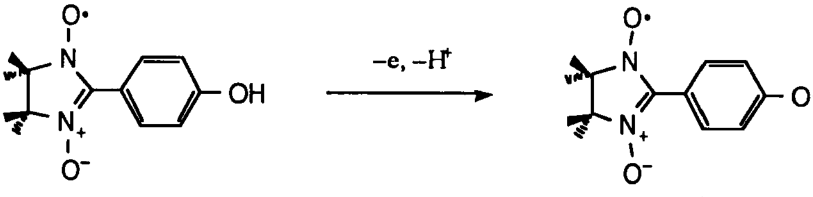
We also examined the radiolyses of **9** (R = H and *p*-MeOC$_6$H$_4$) and **11** (R = *p*-Me$_2$NC$_6$H$_4$), but the ESR spectra of the radicals were merely reduced without the appearance of signals due to biradicals. Thus, it seems to be difficult to obtain biradicals from these radicals by the simple oxidation as depicted in eq.1.

On the contrary, the ESR spectrum obtained by the radiolysis of *p*-hydroxyphenyl-substituted nitronyl nitroxide **14** exhibited additional signals outside the ESR signal of



14 **15** (6)

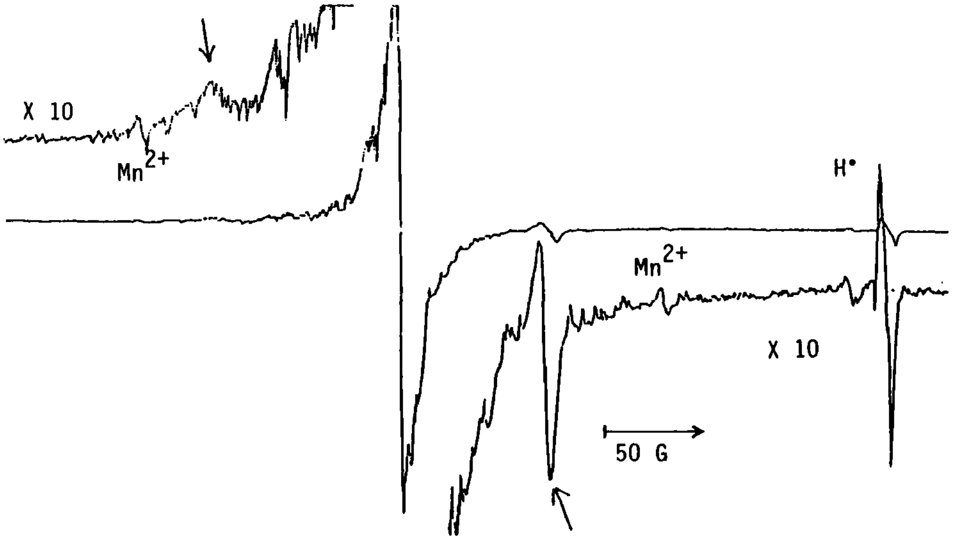
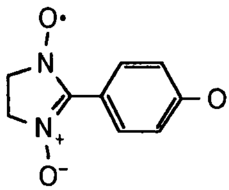


FIGURE 1. ESR spectrum of γ-irradiated **14**-$CFCl_3$ at 77 K.

starting radical as shown in Figure 1. The peaks observed at 3180, 3210, and 3330 G may be possibly assigned to those of a triplet biradical **15** formed by the oxidation followed by the deprotonation of **14** (eq.6). In accord to the assumption, the semiempirical PM3-CI (6 electrons in 5 orbitals) calculation for **16** placed the triplet state 11.4 kcal/mol lower than the singlet.



16

In contrast to other radicals, the radiolysis of **14** was quite inefficient. This may be due to the low solubility of **14** in $CFCl_3$ since it seems that most of **14** crystallize upon cooling. Thus, we could not obtain more definitive ESR spectrum at present.

The cyclic voltammogram of **14** obtained in MeOH or MeCN at room temperature was reversible and practically identical to that of **11** (R = Ph). This means that **14** is oxidized to give the cation similar to **12** and does not deprotonate in polar solvents. However, the addition of 1 equivalent NaOMe resulted in the appearance of an irreversible oxidation peak at lower potential (~ +0.5 V), which was close to that of phenoxide ion.[17] The voltammogram became completely irreversible in the presence of excess amount of NaOMe, indicating that **15** is not stable in solution. Thus, the environment for deprotonation seems to be important for the biradical formation, and the ferromagnetic coupling may be expected for **14** with acceptors if a cooperative proton-electron transfer occurs between them in solid phase.[8]

REFERENCES

1. E. J. Gabe, J. R. Morton, K. F. Preston, P. J. Krusic, D. A. Dixon, E. Wasserman, and J. S. Miller, J. Phys. Chem., 93, 5337 (1989), and references cited therein.
2. H. M. McConnell, Proc. R. A. Welch Found. Chem. Res., 11, 144 (1967).
3. C. Kollmar and O. Khan, J. Am. Chem. Soc., 113, 7987 (1991).
4. K. Awaga, T. Sugano, and M. Kinoshita, Chem. Phys. Lett., 141, 540 (1987).
5. Y. Nakamura, N. Koga, and H. Iwamura, Chem. Lett., 69 (1991).
6. D. A. Kaisaki, W. Chang, and D. A. Dougherty, J. Am. Chem. Soc., 113, 2764 (1991).
7. F. G. Bordwell and J.-P. Cheng, J. Am. Chem. Soc., 111, 1792 (1989).
8. K. Nakasuji, K. Sugiura, T. Kitagawa, J. Toyoda, H. Okamoto, K. Okaniwa, T. Mitani, H. Yamamoto, I. Murata, A. Kawamoto, and J. Tanaka, J. Am. Chem. Soc., 113, 1862 (1991).
9. N. Kato, T. Miyazaki, K. Fueki, N. Kobayashi, K. Ishiguro, and Y. Sawaki, J. Chem. Soc., Perkin Trans. 2, 881 (1987).
10. G. D. Mendenhall and K. U. Ingold, J. Am. Chem. Soc., 95, 2963 (1973).
11. J. H. Wieringa, H. Wynberg, and J. Strating, Tetrahedron, 30, 3053 (1974).
12. Y. Inagaki, R. Okazaki, and N. Inamoto, Bull. Chem. Soc. Jpn., 49, 1142 (1976).
13. K. Ley, E. Müller, and K. Scheffler, Angew. Chem., 70, 74 (1958).
14. R. Kuhn and H. Trischmann, Angew. Chem., 75, 294 (1963).
15. E. F. Ullman. J. H. Osiecki, D. G. B. Boocock, and R. Darcy, J. Am. Chem. Soc., 94, 7049 (1972).
16. D. G. B. Boocock and E. F. Ullman, J. Am. Chem. Soc., 90, 6873 (1968).
17. F. G. Bordwell and J.-P. Cheng, J. Am. Chem. Soc., 111, 1736 (1989).