Communications to the Editor

- (6) T. Kawamura, S. Matsunami, and T. Yonezawa, Bull. Chem. Soc. Jpn., 40, 1111 (1967).
- (7) E. G. Janzen, B. R. Knauer, L. T. Williams, and W. B. Harrison, J. Phys. Chem., 74, 3025 (1970), and references cited therein.

Paul H. Kasai*

D. McLeod, Jr.

Union Carbide Corporation Tarrytown Technical Center Tarrytown, New York 10591

Received October 3, 1977

Radiation Damage in Solid 5-Halouracils. Electron Spin Resonance of Single Crystals of 5-Bromouracil

Publication costs assisted by the Universität Regensburg

Sir: In their first ESR study of single crystals of 5halouracil derivatives, Hüttermann and Müller¹ noted rather complex, highly anisotropic line features obtained upon irradiation of single crystals of the base 5-bromouracil (BU) at 300 K. Lack of knowledge of the crystal and molecular structure of this compound as well as of the characteristics of hyperfine interaction with halogen nuclei prevented a detailed assignment at that time. A radical resulting from loss of a hydrogen from N₁ (structure I) was



proposed tentatively, since some of the observed lines seemed to indicate an interaction of the unpaired electron with $^{14}\rm N$ and $^{79,81}\rm Br$ nuclei.

Since then, we have studied radiation-induced free radicals formed in a variety of 5-halouracil bases: riboand deoxyribosides containing chlorine, bromine, and iodine substituents.² The knowledge gained about halogen hyperfine interaction together with the availability of crystal structure data for BU enable us now to confirm the assignment of I as the dominant radical at 300 K and to present details of its spectral parameters.

The experimental procedures for growing of single crystals, x irradiation, ESR data acquisition, and numerical spectra simulation were as described previously.^{1,2} Single crystals of BU are monoclinic, space group $P_{2_{1/c}}$ and contain four molecules in the unit cell. The molecules are coplanar, their C-Br bonds being aligned parallel and antiparallel, respectively.³

Figure 1 gives the ESR spectra for the direction of the magnetic field parallel to the normal of the molecular planes (\vec{x} direction) obtained at X- (9.5 GHz) and Q-band (35 GHz). These spectra are identical with those of Figure 7 of ref 1. Apart from a superimposed central singlet or doublet line group, all observed lines can be accounted for by assuming hyperfine interaction of the unpaired electron with ¹⁴N and bromine nuclei. Theoretical spectra simulation using the parameters given in Table I reveal that the isotopic splitting due to ⁷⁹Br and ⁸¹Br nuclei (natural abundance 1:1) is not distinguishable in the two outermost ($m_I = \pm 3/2$) hyperfine transitions. Thus, the decrease in hyperfine coupling for ⁷⁹Br isotopes ($\mu^{79}\text{Br}/\mu^{81}\text{Br} = 0.93$) is, for the outermost transitions, compensated for by their larger nuclear electric quadrupole moment (eqQ¹⁹Br/eqQ⁸¹Br = 1.18).

Figure 2 shows the ESR spectra for the other two

 $\underline{BU} H_0//\overline{X} 9.5 \text{ GHz}$ Radical (1) $\frac{d_N}{d_{27BP}}$ $\frac{20G}{35 \text{ GHz}}$ $\frac{20G}{d_{7BP}}$



a_{nBe}



Figure 2. ESR spectra (first derivative) of BU crystals x irradiated at 300 K. Magnetic field is oriented along \vec{z} (left) and \vec{y} (right). Observation at X- (top) and Q-band (bottom) frequencies. Simulated line positions and intensities of radical I are given as stick spectra. Contribution of radical II is indicated as stick diagram below spectrum top left (\vec{z}).

canonical orientations of radical I. Along \vec{z} , the magnetic field is oriented parallel to the C–Br bond yielding a first-order quartet line group of even spacing for both ⁷⁹Br and ⁸¹Br isotopes. The in-plane ¹⁴N hyperfine interaction is not resolvable. With the magnetic field in the molecular plane but perpendicular to the C–Br bond (\vec{y} direction) an unevenly spaced quartet arising from bromine $\Delta m_I =$ ±2 nuclear transitions is observed. Simulated stick spectra indicate the presence of $\Delta m_I = 0$, ±1 transitions as weak outer satellites.

Table I lists the spectral parameters of radical I used to simulate the canonical spectra. Further proof of their validity was obtained from simulation of a crystal rotation from \vec{x} to \vec{z} which gave excellent agreement with experimental spectra. The sign of the hyperfine interaction was

0022-3654/78/2082-0621\$01.00/0



Figure 3. X-band ESR spectra of BU powder x irradiated at 300 K and observed directly after irradiation (top) and after about 3 weeks storage (bottom).

TABLE I: Spectral Parameters of Radical I in BU Single Crystals Obtained from Spectra Simulation^a

Isotope	Hyperfine interaction, ^b G	Nuclear quadrupole interaction, MHz	g tensor
⁸¹ Br	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$-32 \\ -32 \\ 64$	1.998 2.025 2.031
⁷⁹ Br	xx 105.8 yy -28.8 zz -24.8	-37.8 -75.6 75.6	2.001
¹⁴ N	$\begin{array}{rcr} & 24.0 \\ xx & 13.5 \\ yy & \simeq 0 \\ zz & \simeq 0 \end{array}$		

^{*a*} The Hamiltonian is $\mathcal{H} = \beta \overrightarrow{HgS} + \overrightarrow{S}A_{Br}\overrightarrow{I} + \overrightarrow{S}A_{N}\overrightarrow{I} + \overrightarrow{IP}_{Br}\overrightarrow{I}$ $-(g_{N}\beta_{N}HI)_{Br} - (g_{N}\beta_{N}HI)_{N}$. ^b 10 G \approx 1 mT.

established according to the procedures described previously.²

The powder spectrum of BU taken directly after x irradiation at 300 K is shown in Figure 3 (top). The \vec{x} features of radical I are clearly visible in the outer wings but appear superimposed by \vec{x} lines of another radical also involving bromine hyperfine interaction. These most probably belong to the hydrogen-addition radical II the lines of which are also observed in the single crystals albeit in much lower concentration (cf. Figure 2, top left spectrum). Storage of the powder results in decay of the lines of II (Figure 3, bottom).

Radicals of type I are frequently observed in pyrimidine base constituents of nucleic acids as well as in some of their 5-halogen substituted analogues.^{2c,5} They are considered to be produced from the primary oxidation product (cation) by deprotonation at N1. Glycosidic bond formation in nucleosides (-tides) is known to inhibit their formation.4

Acknowledgment. The assistance of Dr. E. Haindl in computing some spectra and the valuable discussions with H. Riederer concerning powder spectra are gratefully acknowledged. Financial support for this study has been obtained from the Deutsche Forschungsgemeinschaft (Hu 248/1, Hu 248/3).

References and Notes

J. Hüttermann and A. Müller, *Int. J. Radiat. Biol.*, **15**, 297 (1969). (a) J. Hüttermann, W. A. Bernhard, E. Haindi, and G. Schmidt, *Mol. Phys.*, **32**, 1111 (1976); (b) J. Hüttermann, G. W. Neilson, and M. C. R. Symons, *Ibid.*, **32**, 269 (1976); (c) H. Oloff and J. Hüttermann, *J. Magn. Reson.*, **27**, 197 (1977); (d) E. Haindi and J. Hüttermann, *Ibid.*, bross. (2) ibid., in press.

Communications to the Editor

 (3) H. Sternglanz and C. E. Bugg, *Biochem. Biophys. Acta*, **378**, 1 (1975).
(4) A. Müller, and J. Hüttermann, *Ann. N.Y. Acad. Sci.*, **222**, 411 (1973). (5) R. A. Farley and W. A. Bernhard, Radlat. Res., 61, 47 (1975).

Institut für Biophysik und Physikalische Biochemie Jürgen Hüttermann* Universītät Regensburg Postfach 397 D-8400 Regensburg, West Germany Department of Chemistry

University of Leicester Leicester LE1 7RH, England Martyn C. R. Symons

Horst Oloff

Received November 28, 1977

The Excited State Lifetime and Metal to Ligand **Charge Transfer Photochemistry of the**

Tris(blpyridine)iron(II) Ion Probed Electrochemically

Publication costs assisted by the National Research Council of Canada

Sir: The study of photoinduced electrode reactions has recently emerged as an area of vigorous activity in inorganic photochemistry. Several groups have reported¹⁻³ large (or "supersensitized") photocurrents arising in the presence of scavengers. These large currents arise when scavengers convert excited states into longer lived, thermally relaxed, reactive intermediates which subsequently react at the electrode. The scavenging of the excited state of $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$ (bpy = bipyridine) by Fe^{3^+} gives $\operatorname{Ru}(\operatorname{bpy})_3^{3^+}$ and Fe^{2^+} . A large *cathodic* current arises from reaction of $\operatorname{Ru}(\operatorname{bpy})_3^{3+}$ at various electrodes such as SnO_2 and TiO_2 .¹⁻³

We have pointed out³ that the Fe³⁺ concentration dependence of scavenging arises from the ratio of the rate constant for reaction between the Ru(II) excited state and Fe^{3+} and the rate constant for relaxation of the Ru(II) excited state. If the rate constant for the scavenging reaction can be estimated, the lifetime of the excited state can be extracted without reference to luminescence decay measurements. Since reactions of excited states are commonly highly exothermic, arguments based on Marcus theory⁴ can be employed to show that it is appropriate to assign a diffusion-limited rate constant to the scavenging reaction. With diffusion-limited rate constants chosen according to accepted theory,⁵ a rate constant for relaxation of the Ru(II) excited state was calculated³ in excellent agreement with values derived from luminescence decay. This approach offers the opportunity to estimate excited state lifetimes of nonluminescent compounds. This communication discusses the photochemistry and excited state lifetime of $Fe(bpy)_3^{2+}$ which has not been reported to luminesce.

Our experiments used a 4-W Spectra Physics Ar ion laser as a source of radiation between 459 and 514 nm at the wavelengths indicated in Figure 1 with an intensity of 100 or 200 mW. Irradiation was through a doped SnO_2 electrode with 80% transmittance and a resistance of 80 ohm m⁻². Potentials were set relative to SCE with a Wenking potentiostat. The laser beam was chopped at 30-200 Hz and current detected with a PAR lock in amplifier. Small anodic photocurrents in the absence of scavengers which are related to direct reaction of Fe- $(bpy)_3^{2+}$ excited state at the electrode will be described in detail elsewhere.⁶ The earlier literature on this subject has been evaluated.⁷

In the presence of concentrations of Fe^{3+} between 0.012 and 0.050 mol dm⁻³ at pH 2.0, large cathodic photocurrents