Advances in

Photochemistry

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(Editors)

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Editors

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Foreword

Volume 1 of this series, Advances in Photochemistry, appeared in 1963. The stated purpose of this series was to explore the frontiers of photochemistry through the medium of chapters written by pioneers who are experts. Frontiers in photochemistry are at times full of confusion and for this reason they are fascinating!

In the first eight volumes the editors have not acted as censors. We have followed the principle set forth in the original introduction to this series, that is, "the authors are free to make any statement they wish which cannot be proven wrong." We have solicited articles from experts who have strong personal points of view concerning fundamental aspects of photochemistry and spectroscopy. We have asked these authors to present their points of view through critical discussion and evaluation of existing data. In no sense have the articles been simply literature surveys although in some cases they have fulfilled both purposes.

We trust that during the past few years, when photochemistry has truly come of age, that this series has proven to be stimulating and has served our original purpose of bringing together points of views of photochemists and spectroscopists who only a short five to ten years ago did not even use the same vocabulary.

Two of us welcome the addition of Dr. Klaus Gollnick as an editor and hope that this will give even better coverage to the "European photochemical scene." We intend to continue the policies as established in the previous volumes.

The present editors wish to express their deep gratitude to Professor W. Albert Noyes, Jr., who served with two of us as co-editors of the first eight volumes of this series. Professor Noyes' wise guidance and his willingness to read and work with manuscripts was invaluable to the success of the series. The field of photochemistry has profitted in many ways and for many years from the

inspiration and hard work contributed by Professor Noyes.
It has been a privilege and source of personal satisfaction
to have worked with him in this enterprise.

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Application of Electron Spin Resonance Spectroscopy to Photochemistry

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I. INTRODUCTION

Most, if not all, photochemical systems involve the formation and reactions of electronically excited molecules, free radicals, or atomic transients. The study of a photochemical reaction involves the elucidation of the primary process and of all secondary reactions which follow. The determination of the mechanism of a photochemical reaction requires ideally the identification

of each elementary reaction occurring, together with a
quantitative assessment of the role which each step plays
in the overall reaction. In recent years an increasing
number of photochemists have focused their attention on
the relationships between molecular and electronic
structures of excited molecules and free radicals and
their chemical reactivities in photochemical systems.

Historically the most popular method for studying
photochemical reactions is the "product analysis" method
which involves a process of deduction based on obser-
vations of the overall behavior. However, such a method
cannot provide unequivocal evidence for the existence of
free radical intermediates, let alone information on
their structures. The development of flash photolysis
since the 1940s has proved to be a general and perhaps
the most powerful of all techniques in photochemistry (1).
Coupled with UV-visible spectroscopy, the flash method
permits direct observation of transient intermediates
and their kinetic behavior. Difficulty is sometimes
encountered in specific systems with the optical detection
technique. For example, the identification of CH_3
radicals in the flash photolysis of gaseous $(CH_3)_2Hg$ has
been complicated by the fact that the transitions in the
near UV and visible region are forbidden due to the
geometry of the radical (2). When the flash method is
applied to condensed phase systems, high resolution
absorption spectra of the transients are difficult to
obtain. Great care must also be taken to differentiate
possible spurious absorption due to impurities and
solvent radicals. In recent years the flash photolysis
method has been coupled to various specifically designed
detection systems including time-resolved mass
spectrometry (3), photoconductivity (4), rapid scan

infrared spectroscopy (5), and rapid scan electron spin
resonance spectroscopy (6).

Since 1945 the development of electron spin
resonance (ESR) spectroscopy, more satisfactorily known
as electron paramagnetic resonance, has proved exceedingly
useful for the study of paramagnetic molecules. It
concerns magnetic dipole transitions between Zeeman
energy levels of any system that possesses electronic
magnetic moments. Systems that usually respond to ESR
study include atoms with an odd number of electrons, ions
having partly filled inner electron shells, and other
molecular species that possess electronic angular
momentum. It should be noted that some free radicals
having unpaired electrons may not invariably show ESR
phenomena and some diatomic molecules containing no
unpaired electrons can be readily studied by ESR. The
best known example of the first case is the $^2\pi_{1/2}$ state of
NO which has no magnetic moment although it is a doublet
state with an unpaired electron. An example of the
second case is molecular oxygen in the $^1\Delta_g$ state which
has no unpaired electron but possesses orbital angular
momentum. However, similar exceptions are rare among
polyatomic systems, and for practical purposes we
consider that the technique of ESR can be potentially
applied to studies of all polyatomic radicals.

In recent years the state of the art in ESR
instrumentation has matured enough that the technique is
being used more and more by photochemists to elucidate
the structure and reactivity of free radicals and organic
triplet molecules in photochemical systems. Indeed, a
renewed and increasing interest in the field of free
radical chemistry during the last decade can be attributed
mainly to the rapid development of electron spin resonance

spectroscopy. The technique is very versatile as it can
be applied to gaseous, liquid, or solid systems over a
large range of temperatures. In the past most photo-
chemical systems studied by ESR were in the condensed
phase and usually involved reactions in the steady state.
Nevertheless, ESR studies have contributed significantly
to photochemistry. It is clearly not feasible to present
here a detailed review of all aspects of the enormous
amount of work which has been done in this field. Rather,
we shall aim at general illustrations of the application
of ESR to a variety of photochemical systems and
discussions of some of the current development in the
study of fast free radical reactions.

II. SOME REQUISITE THEORETICAL BACKGROUND
IN ESR SPECTROSCOPY

The first experimental observation of electron
spin resonance was made on an iron compound by Zavoisky in
Russia in 1944. A year later Purcell and Bloch and their
collaborators observed independently nuclear magnetic
resonance in condensed matter. While the celebrated
Purcell and Bloch discoveries have sparked an explosive
wave of research on nuclear magnetic resonance throughout
the world, little activity on electron spin resonance
followed immediately after the first success. In fact,
even Zavoisky did not continue working in the field of
ESR, and the development of the technique was almost
exclusively left to the physicists in the decade after
the war. Indeed, the potential diversity of applications
of ESR to chemistry could hardly have been foreseen in
the earlier days.

The basic theory of the phenomenon of electron
spin resonance was developing even before the first

experimental observation. Formal and rigorous intro-
duction of all aspects of the theory have been documented
in many excellent monographs (7) on ESR published in the
last decade. Obviously the kind of ESR information the
photochemist seeks can be quite different from that
required by the physicist. In general the photochemist is
interested in the detection and identification of radicals
and photoexcited molecules and in analyzing their molecular
structure and quantitative kinetic behavior. The intention
of this section is merely to briefly summarize several
important points which should be remembered in inter-
preting ESR data of interest to the photochemist.

A. Magnetic Properties of Radicals, Molecules, and Excited Molecules

The photochemist's first concern is whether or not
a particular transient in a photochemical reaction can be
detected by ESR under certain experimental conditions.
This requires the knowledge of the magnetic properties
of the species in question. Atoms having odd numbers of
electrons are paramagnetic and we will not consider them
here.

Let us first consider the species known as free
radical. Since Lavoisier coined the term "radical" at
the end of the 18th century, it has become one of the
most popular terms in chemistry. Thus a free radical has
generally been defined as "a molecule, or part of a molecule
in which the normal chemical binding has been modified so
that an unpaired electron is left associated with the
system."(8). It has also been widely recognized that
free radicals usually have a high chemical reactivity,
but "stable radicals" which can be isolated in well-
defined liquid or crystalline form are well known.

For a radical to be detected by ESR, it must possess

a magnetic moment originating from its unpaired electron.
First-order contributions to the magnetic dipole moment
μ may arise from the electronic orbital and spin angular
momenta as well as from the rotation of the whole radical.
In general an orbital magnetic moment will occur only in
a state with twofold or more orbital degeneracy. Since
the Jahn-Teller theorem shows that degenerate states in
nonlinear molecules are normally unstable, most poly-
atomic organic radicals have zero orbital magnetic
moment, and their magnetic moments arise mainly from
spin and can be expressed as

$$\mu = -g_e \beta_e \underline{S} \tag{2-1}$$

where $\underline{S}$ is the dimensionless spin vector of magnitude
1/2 $\hbar$ which gives the intrinsic spin angular momentum of
the unpaired electron; β_e is the Bohr magneton, and g_e
the free electron g-factor which has the value 2.00232.

It should be noted that several aromatic hydro-
carbon ions with an unpaired electron and threefold or
higher axis of symmetry, such as $C_6H_6^+$ and $C_6H_6^-$ are known
to have orbitally degenerate ground states. Linear
radicals with orbital moments, such as NO, OH, SH, NCO,
and NCS, are also well known. In the case of NO, it has
a $^2\pi_{1/2}$ ground state, and the magnetic moment in this
state is given by

$$-\mu = \beta_e \Lambda + g_e \beta_e \underline{S}$$

$$= (1 - 1/2g_e) \beta_e$$

$$= -0.00116 \beta_e \tag{2-2}$$

and NO is often referred to as having zero moment.
Another state of NO, $^2\pi_{3/2}$, lies 121.1 cm^{-1} above the
ground state and has a moment $\mu \simeq -2\beta_e$. Thus at room

temperature both states are populated and NO can be detected by ESR. As the temperature is lowered, the relative population in the paramagnetic $^2\pi_{3/2}$ state is greatly reduced, and the magnetic moment of NO tends almost to zero at very low temperatures.

We have so far implied that radicals are species with an odd number of electrons. We now turn to molecules having an even number of electrons. Organic molecules in their ground state with an even number of electrons almost invariably have no orbital magnetic moment. Spin magnetic moments can, however, arise in some ground state molecules with an even number of electrons. This usually occurs in molecules which have a triplet ground state. The most common example is the ground triplet state of molecular oxygen. In recent years an increasing number of interesting molecules including methylene and its derivatives, nitrene derivatives, the species CNN, NCN, and NCCCN have been studied by ESR and their triplet ground state confirmed (9). In addition, aromatic hydrocarbons with three- or six-fold symmetry, such as triphenylene and decacyclene, may form dianions, with a triplet ground state (10). For the present we shall regard a triplet state molecule as having two "odd electrons."

Molecules with triplet ground states may have low-lying metastable electronic excited states with different multiplicity, symmetry, and magnetic properties. For example, the triplet methylene is bent and paramagnetic while the excited singlet methylene is linear and dia-magnetic. Their chemical reactivities are also known to be different (11). Another example is molecular oxygen in which the two low-lying singlet excited states $^1\Delta_g$ and $^1\Sigma g^+$ have significantly different chemical (12,13)

and magnetic properties from those of the ground triplet state $^3\Sigma g^-$. Thus the $^3\Sigma g^-$ state has a spin magnetic moment; the $^1\Delta g$ excited state possesses no unpaired electrons, and its magnetic moment arises mainly from electronic orbital angular momentum; and the $^1\Sigma g^+$ excited state is diamagnetic.

Molecules with a singlet ground state may have an electronically excited triplet state accessible by photoexcitation via a radiationless intersystem crossing. Indeed, photochemical study of excited triplet states coupled with ESR spectroscopy is perhaps one of the most exciting chapters in the recent advances in photochemistry.

B. Electron Spin Interactions: A Source of Chemical Information

In addition to the capability of detecting very low concentration of free radicals as transients in a chemical reaction, ESR spectroscopy provides experimentally the following very important sources of chemical information on their structure. (a) The resonant position referred to as the g value is directly determined by the separation of the energy levels of the radical under investigation. Variation of the g value is interpreted in terms of the perturbation by the spin-orbit interactions, and may be used as a probe to study substitution effects and changes in molecular structure (14,15). (b) The width and shape of the ESR lines are determined by the relaxation of the spin energy state. Elucidation of the various interactions which contribute to the relaxation provides very valuable information on the behavior of the unpaired electron (16). (c) The hyperfine structure of ESR spectra is produced by the interaction of the electron spin magnetic moment with the magnetic moments of the nuclei contained by the molecular orbital of the unpaired

electron. Well-resolved hyperfine patterns often help to "fingerprint" the radicals under investigation and also reveal information regarding the spin densities at the various sites in the molecule and their correlation with the chemical nature of bonding. (d) For systems with more than one unpaired electron, such as triplet states, the interaction between two unpaired electrons leads to fine structure in the ESR spectra and provides a wealth of information concerning the electronic structures and the dynamics of the triplet state molecules. We will not consider here interaction between the electron spin and the molecular rotational magnetic moment. Spin-rotation coupling is important mainly in the gas phase ESR study of simple radicals at very low pressures, and the inter-pretation of this coupling in ESR spectra is beginning to be understood (17,18).

1. Electrons in Magnetic Fields

In a magnetic field $\underline{H}$ the energy of interaction $\underline{W}$ with the electron spin moment is given by

$$\underline{W} = -\mu \cdot \underline{H} \tag{2-3}$$

and for a field $\underline{H}$ along the z direction the degenerate eigenstates with $\underline{m}_s = \pm 1/2$ split into a lower level $\underline{m}_s = -1/2$ and a higher level $\underline{m}_s = 1/2$ separated by an energy $g_e \beta_e \underline{H}$. The relative population of these two states in thermal equilibrium and in the absence of other polarization effects is governed by the Maxwell–Boltzmann distribution. Transitions between these two energy states $\underline{m}_s = 1/2$, $\underline{m}_s = -1/2$ can be equally induced by applying an alternating field having its magnetic component perpendicular to the constant magnetic field and its frequency ν being equal to $g_e \beta_e \underline{H}/h$. The transition probability for a free spin has been treated both by the Heisenberg method and by the perturbation theory for the

coupling of the spin with the rotating field (7a). Since
the probabilities of these transitions are equal and the
equilibrium population of the lower state is slightly
higher than that of the upper state, there will be a net
absorption of the energy of the rotating field.

Experimentally the possibility of observing the
transitions depends on the population difference between
the two spin states, and the lifetime of the upper state
which is determined by the spontaneous emission probability
and by the various relaxation processes available. ESR
emissions have been observed (19) in several systems in
which the upper spin state has a higher population.
The lifetime of the upper state as determined by the
probability of spontaneous emission between the two spin
levels can be calculated from the Einstein coefficient
$\underline{A}_{1/2 \to -1/2}$:

$$\underline{A}_{1/2 \to -1/2} = \frac{32\pi^3 \nu^3}{3c^3 h} \, g_e^2 \beta_e^2 \qquad (2-4)$$

In a magnetic field of 10,000 gauss, the resonance
frequency ν of the free electron (g = 2.0023) is 28,026
Mc/s and the spontaneous emission lifetime is $\sim 10^{13}$ sec.
Obviously this lifetime is too long and the transitions
will be saturated exceedingly easily. In other words,
the populations of the two levels become essentially
equal and no net transition can be observed. Fortunately
there are a number of nonradiative relaxation mechanisms
open to the upper spin level including interactions with
other electrons, with nuclei having nuclear magnetic
moments, and with the lattice. The latter process is
often known as spin-lattice relaxation. The term "lattice"
generally refers to the degrees of freedom of the system
other than those directly related with spin. Spin