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Deciphering mechanism of excited state reactivity by spectroscopic methods

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ABSTRACT

The Feature highlights Electron Paramagnetic Resonance (EPR) spectroscopy as an indispensable tool to understand the excited state reactivity of organic molecules.

1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy, since its discovery by Zavoisky in 1944 [1], rapidly grew over the next two decades to be the most powerful technique for the study of radicals and radical ions [2]. By the mid-1960′s most chemistry and physics departments in major research institutions owned commercial spectrometers and began to hire specialists in the field. Simultaneously, there began an exploration of organic photochemistry, and in particular the properties of photoexcited triplet states, during this same time period [3–5]. It can hardly be a coincidence that Lewis and Kasha's studies of the energy levels and luminescent properties of purported triplet states were published at almost exactly the same time [6]. This deep connection between organic excited state properties and the structure, dynamics, and reactivity of the ensuing free radicals continues into the modern era, and holds promise for future applications in molecular magnetism, quantum information science, and understanding the role of reactive oxygen species in human diseases [7]. In this Feature we highlight the use of a specific EPR methodology known as spin trapping, demonstrating its ability to provide high resolution structural data for free radicals, combined with high sensitivity and detailed information about their excited state precursors.

Steady–state EPR spectroscopy (SSEPR) is carried out with a DC electromagnet to create the Zeeman effect, which splits the energy levels of the unpaired electron, and balanced microwave bridge that sends and receives radiation to and from a tuned resonator containing the sample [5]. Changes in the reflected power of the source upon resonant absorption are detected as DC offsets from the baseline. Because the detector is set up for "lock in" amplification of signals responding to an applied field modulation (typically 100 kHz), SSEPR signals appear in first derivative mode, i.e., the typical line shape is one where an absorptive transition grows immediately above the baseline, maximizes, then minimizes, and finally returns to a flat baseline. Fig. 1 (left side) shows the application of the field modulation method and the resulting first derivative line shape for the well-known TEMPO stable nitroxide free radical.

Hyperfine splitting patterns arise due to interactions between the unpaired electron spin and neighbouring spin-active nuclei such as protons (total spin ½) and nitrogens (total spin 1, as shown for TEMPO in Fig. 1)) [5]. The high resolution structural information in EPR can be of great utility in analyzing reactive intermediates created during photochemical reactions, particularly from photoexcited triplet states. Another parameter that can be varied is the field/frequency of operation of the EPR spectrometer. Similar to NMR spectroscopy, at higher fields and frequencies of excitation, better spectral resolution and higher sensitivity often result. The most common EPR commercial spectrometers operate at X-band (9.5 GHz) and Q-band (35.5 GHz) [8].Comparisons of spectra at each frequency often lead to new information about radical structure and dynamics.

The time resolved EPR experiment (TREPR) [9] is carried out somewhat differently in that the microwave excitation of the EPR signals is still carried out with continuous wave (CW) radiation, the 100 kHz field modulation is dispensed with in order to examine faster (100 ns to 10 μs) phenomena. The sample, usually flowing through the resonator to

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prevent heating, is irradiated with a pulsed laser and the EPR signal is detected in a gated fashion, with one logic gate sampling the transient EPR signal before the laser flash (dark signal) and one after the flash (light + dark). The difference between the two boxcar gate voltages is the light induced EPR signal. The right side of Fig. 1 shows the timing sequence for the TREPR experiment and an example spectrum. Typically, the sampling gates are fixed in time while the magnetic field is swept to collect an entire spectrum. Then the light sampling gate can be moved to a different delay time to collect another spectrum, thus establishing a time dependence for the phenomenon under investigation. The radicals observed in the TREPR spectrum in Fig. 1 arise from the photoreduction of acetone in 2–propanol, leading to two identical 2-propanoyl radicals (structure is shown in Fig. 1). Note that because the 100 kHz field modulation is not used in TREPR spectroscopy, the observed transitions have "normal" Lorentzian line shapes and no longer appear as first derivatives.

TREPR spectra are dominated by, and in fact cannot normally be observed without, the phenomenon of chemically induced dynamic electron spin polarization (CIDEP). These non–Boltzmann populations can be enhanced absorptive (A) or emissive (E) in nature. Such polarization can be generated by several different mechanisms and a detailed analysis of the TREPR signal intensities and line shapes can be very informative about radical pair dynamics and reaction mechanisms [5]. For example, the phase of the TREPR spectrum in Fig. 1 (low field E, high field A) gives direct support for reaction from the photoexcited triplet state of the precursor (the spectrum would be A/E for a singlet precursor). For the 2-propanoyl radical shown, seven lines are predicted and six are observed, three in emission and three in absorption. The central line receives almost equal amounts of E and A polarization, so it has little intensity.

2. Spin trapping strategy

The spin trapping method in EPR spectroscopy has been widely exploited for detecting free radicals and/or intermediates that are not stable and/or have short lifetimes. [10,11] An optimal spin trap should be chemically inert towards non-radical reactive species, and simultaneously reactive enough to trap the free radicals of interest. They should in general not have significant absorption of visible light nor should they be highly photoactive in the UV region. There are several types of spin trapping agents which have been developed over the past four decades [12–15]. The most common types of spin traps are nitrone and nitroso compounds (Scheme 1). Their reactivity with free radicals to form EPR active nitroxides is shown in Scheme 2.

Both types of spin trapping agents form (usually stable) spin adducts that can be studied by steady-state EPR spectroscopy. Nitrones typically react with oxygen-centered radicals more quickly compared to nitroso compounds [2]. However, a nitroso spin adduct can give more information about the attacking radical because the radical is attached directly to the nitrogen atom. In reactions involving nitrones, the radical attaches to the carbon atom at the ß-position (further away from the nitroxide radical center), giving less specific information about the attacking species. The trapped radical from the nitrone or nitroso compound (a nitroxide) gives information in the EPR spectrum such as the g-factor (chemical shift) of the unpaired electron, and the hyperfine splitting constant $\boldsymbol{a}$. The g-factors of most nitroxides are very similar (2.005–2.006) [16] and are thus less informative. Based on hyperfine splitting constants, the trapped radicals can be identified or distinguished from each other in different experiments or experimental conditions. The number of lines resulting from interaction of an unpaired electron with surrounding nuclei with a spin number of **I** is equal to $\mathbf{2I+1}$. For example, in the DMPO spin adduct (Scheme 1, top) the unpaired electron interacts with a single nitrogen atom which has a total spin of 1. Therefore, the signal splits into three lines due via the maximum number of lines predicted as 2I+1. Further, each of those three lines are split into two by the neighboring hydrogen atom (total spin 1/2) at the ß-position, [17,11] resulting in total of six lines (Scheme 3). However, the ß-H splitting is strongly dependent on the type of atom at the radical center. For example, carbon-centered radicals lead to adducts which typically have hyperfine splitting constants 20–24 Gauss (G), oxygen-centered radicals lead to adducts with $\boldsymbol{a}$ = 7–15 G, and nitrogen-centered radicals lead to adducts with $\boldsymbol{a}$ = 14–18 G. [11,18] In this fashion, the nature of the attacking radical can be deduced, adding mechanistic insight to the analysis of the reaction under investigation.

2.1. Conventional spin trapping

In conventional spin trapping a free radical formed during the course of a thermal or photochemical reaction is trapped by a spin trapping agent which is present in excess in the solution (Schemes 1 and 2). The resulting spin adduct is usually more stable at ambient temperatures and has a long enough lifetime to be detected by steady-state EPR

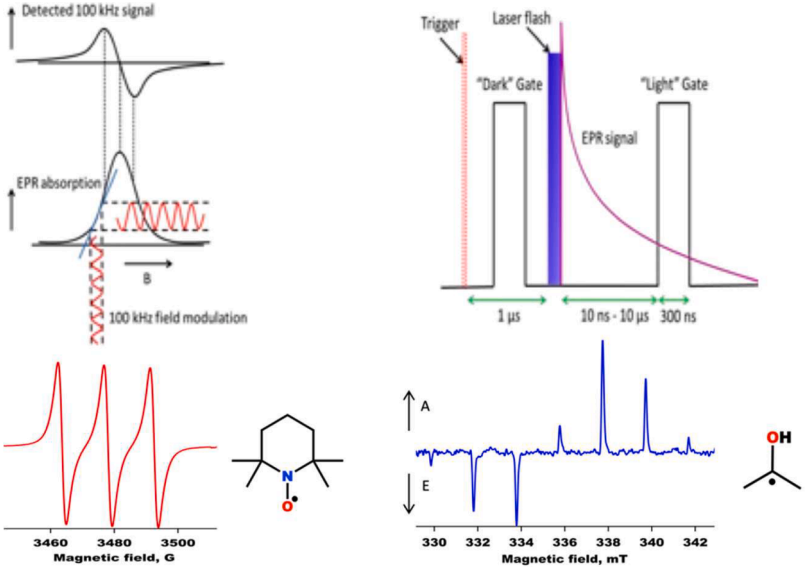


Fig. 1. Steady state (left) and time-resolved (right) techniques and associated line shapes in EPR spectroscopy. The radical species observed on the left is the common stable nitroxide TEMPO. The species observed on the right in the TREPR experiment is the 2-propanoyl radical (structure shown in inset).

spectroscopy. While there are numerous reviews of spin trapping in chemistry and biology [11], it is helpful to present some of the more common reactions that can be investigated using the technique. The versatility of the method and examples of different radical species and their characterization are highlighted below. In many cases the hyperfine coupling constants from trapping reactions have been tabulated for easy reference.

One of the initial reports on the detection and identification of short-lived free radicals using the EPR spin trapping technique was carried out by Blackburn and co-workers [14]. They reported the formation of a strong EPR signal from phenylazotriphenylmethane **7** in benzene containing PBN **2** at room temperature. This signal (based on hyperfine splitting) was assigned to a phenyl radical that was trapped by PBN **2** (Scheme 4) [14].

Rosenthal and co-workers(19) reported the excited state reactivity of dibenzyl ketone **9** Fig. 2 which underwent α-cleavage leading to the geminate radical pair rad-**9a**/**9b**. Radical rad-**9b** underwent decarbonylation to produce benzyl radical rad-**9a**. The benzyl radical rad-**9a** was subsequently trapped by 2-methyl-2-nitrosopropane (MNP) **4** leading to spin adduct **10** that gave the following hyperfine splitting constants: $a^N = 15.00$ G and $a_\beta^H = 7.50$ G.

The interaction between the excited states of metallophthalocyanines and organic peroxides was investigated using EPR spectroscopy by Gantchev and co-workers [20]. They employed a metallophthalocyanine as the photosensitizer (Zn-tetra-tert-butyl phthalocyanine ($ZnPc(t\text{-}Bu)_4$)) in benzene that interacted with tert-butylperoxide **11** Fig. 3 leading to the formation of tert-butoxy radical rad-**11**. Rad-**11** was trapped by DMPO **1** that showed the following hyperfine splitting constants: $a^N = 13.40$ G; $a_\beta^H = 7.70$ G; $a_\gamma^H = 1.90$ G.

2.2. Inverted spin trapping mechanism

One of the disadvantages of spin trapping agents is their susceptibility to oxidation. In the inverted spin trapping mechanism, a spin trapping agent is oxidized to form a radical cation and then it is attacked by a nucleophile to form a spin adduct (Scheme 5) [21].

The formation of spin adduct of benzotriazole with PBN **2** by this mechanism was demonstrated by Greci and co-workers [22]. A solution of benzotriazole **13** in DCM was irradiated in the presence of PBN **2** (Scheme 6). Here, the excited molecule of PBN **2** oxidizes another molecule of PBN **2** to form the radical cation of PBN rad-cat-**2**. This undergoes a nucleophilic attack by benzotriazole **13** to generate spin adduct **14** with hyperfine splitting constants: $a^N = 13.70$ G; $a_\beta^H = 1.61$ G; $a_\beta^N = 3.52$ G.

The oxidation of a spin trapping agent has also been achieved using tris(4-bromophenyl) aminium ion, as demonstrated by Eberson [21]. This report details the formation of the PBN-acetoxy spin adduct **16** (with hyperfine splitting constants $a^N = 13.70$ G; $a_\beta^H = 1.66$ G) via formation of radical cation rad-cat-**2**, which was attacked by the acetoxy ion from tetra-butyl ammonium hydrogen diacetate **15** (Fig. 4).

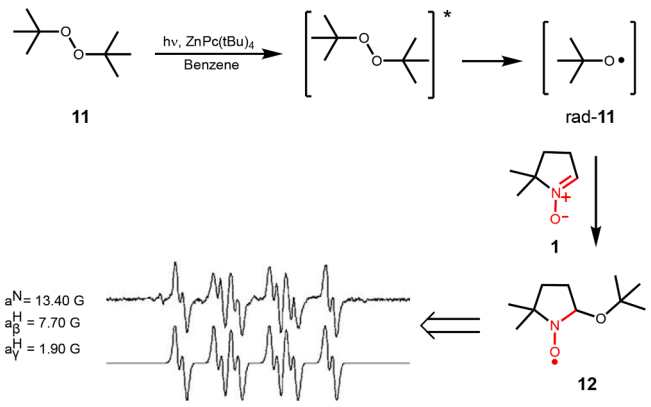


Fig. 3. Experimental (top) and simulated (bottom) spectra of the DMPO/OtBu 12 spin adduct formed by photoirradiation of tert-Butyl peroxide 11 with DMPO 1 in the presence of $ZnPc(tBu)_4$ as a sensitizer in benzene. Reproduced with permission from John Wiley and Sons (reference [20]).

2.3. Forrester–Hepburn mechanism

In 1971 Forrester and Hepburn reported an alternative mechanistic pathway for the formation of spin adducts [23], in which a nucleophile attacks the spin trapping agent followed by the oxidation of the spin adduct leading to a radical (Scheme 7).

Greci and co-workers(22) reported the formation of a spin adduct **18** from benzimidazole with PBN in acetonitrile (Fig. 5) formed by this mechanism. They proposed that the oxidation of benzimidazole **17** by chloranil is not possible due to the large difference in redox potentials. Therefore, a plausible mechanism for the spin adduct formation involved an initial nucleophilic attack of the spin trapping agent **2** by benzimidazole **17** to form anion-**18**, followed by oxidation using chloranil to form spin adduct **18** with the following hyperfine splitting constants: $a^N = 13.67$ G; $a_\beta^H = 2.76$ G; $a_\beta^N = 2.76$ G.

The formation of the DMPO spin adduct from alcohols in the presence of fluoranil via thermal oxidative ability were investigated by Eberson [24]. In this experiment, the appearance of DMPO/OEt **20** in acetonitrile from anion-**20**, which underwent oxidation by fluoranil under dark conditions, was observed. The following hyperfine constants were obtained: $a^N = 13.40$ G; $a_\beta^H = 7.98$ G; $a_\gamma^H = 1.74$ G

Leinisch and co-workers also demonstrated the formation of DMPO-cyanide spin adduct **22** through the Forrester-Hepburn mechanism [25]. They report the formation of hydroxylamine anion-**22** followed by its oxidation by the enzyme horseradish peroxidase to form spin adduct **22** with hyperfine splitting constants: $a^N = 15.42$ G; $a_\beta^H = 18.90$ G (Fig. 7).

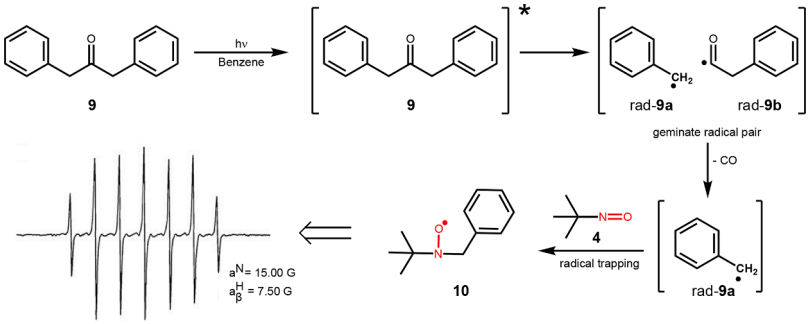
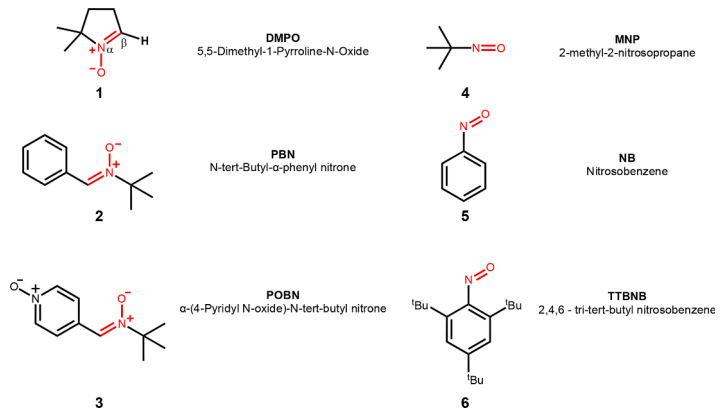
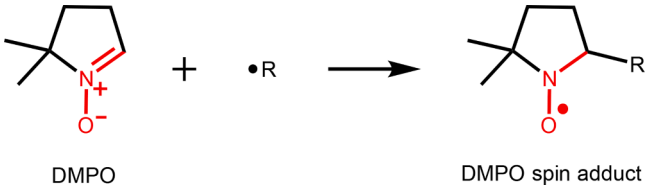


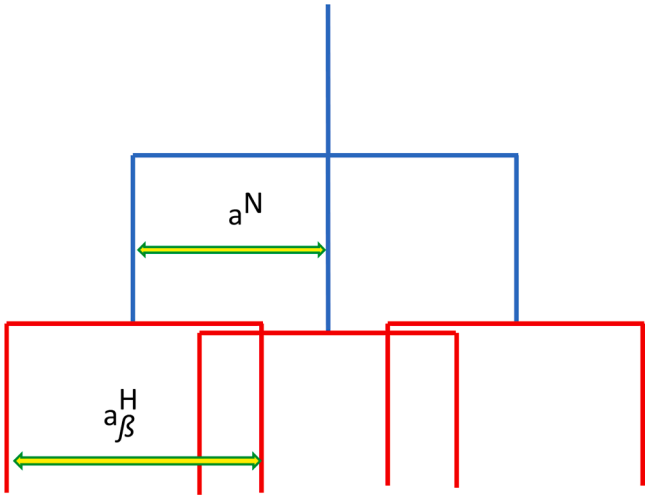
Fig. 2. EPR spectrum of MNP/Benzyl spin adduct 10 in benzene Reproduced with permission from reference [19].



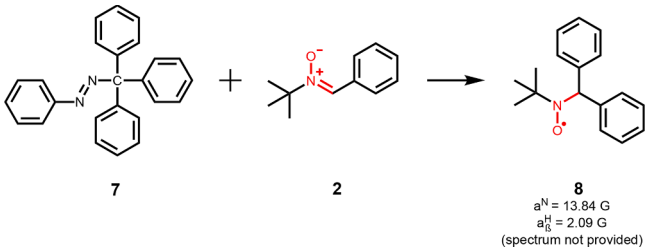
Scheme 1. Commonly used spin trapping agents. Left: Nitrones. Right: Nitroso compounds.



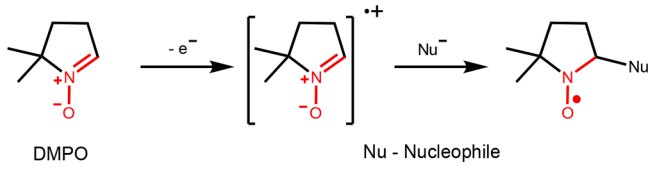
Scheme 2. Conventional spin trapping of radicals by DMPO.



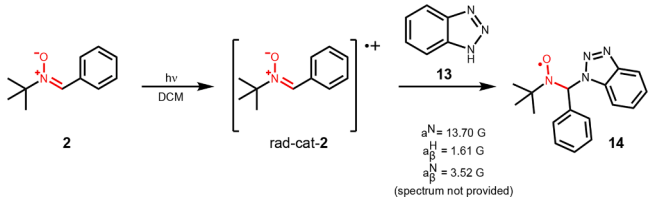
Scheme 3. Stick-diagram of hyperfine splitting constants of nitrogen and ß-hydrogen atoms from the interaction with unpaired electron in DMPO spin adduct.



Scheme 4. Reaction of phenylazotriphenylmethane 7 with PBN 2 in benzene at room temperature to give nitroxide 8 which is easily detected by EPR spectroscopy.



Scheme 5. Inverted spin trapping mechanism involving of nitroxides.



Scheme 6. Irradiation of benzotriazole 13 with PBN 2 in DCM solutions.

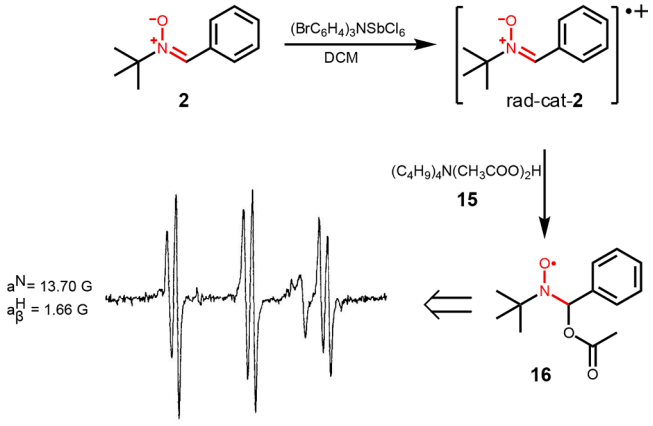
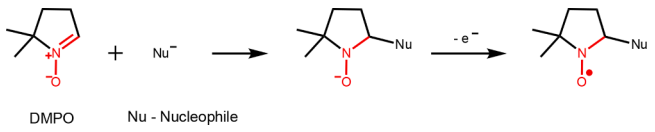


Fig. 4. EPR spectrum of the PBN/acetoxy spin adduct in dichloromethane, produced by reaction of PBN 2 with tetrabutylammonium hydrogen diacetate 15 in the presence of tris(4-bromophenyl) aminium hexachloroantimonate. (Reproduced with permission from the Royal Society of Chemistry (reference [21]).

3. Maleimide as a photochemistry probe

One of the major goals of our research program is to uncover new photoreactions by manipulating excited state pathways [26–31]. One such approach involves employing restricted bond rotations in molecules that are tailored to undergo photochemical transformations [29,



Scheme 7. The Forrester–Hepburn mechanism involving nitroxide.

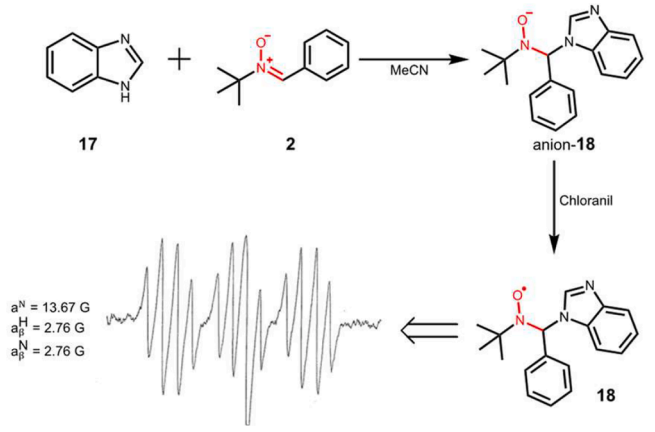


Fig. 5. EPR spectrum of the spin adduct 18 derived from reactivity of benzimidazole 17 and PBN 2 in acetonitrile in the presence of chloranil. Reproduced with permission from the Royal Society of Chemistry (reference [22]).

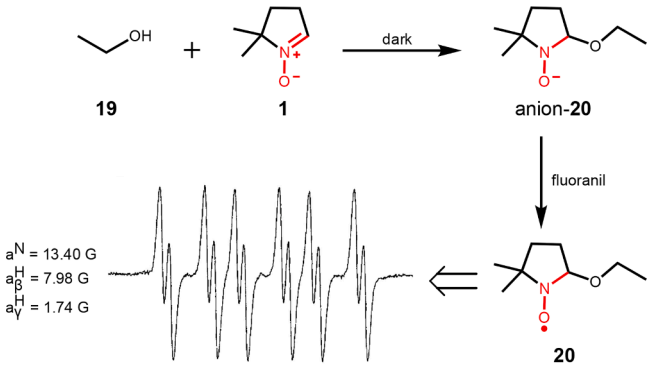


Fig. 6. EPR spectrum of DMPO/OEt spin adduct 20 formed in the dark condition in the presence of fluoranil in MeCN:EtOH (7:1 v/v) solution. Reproduced with permission from the Royal Society of Chemistry (reference [24]).

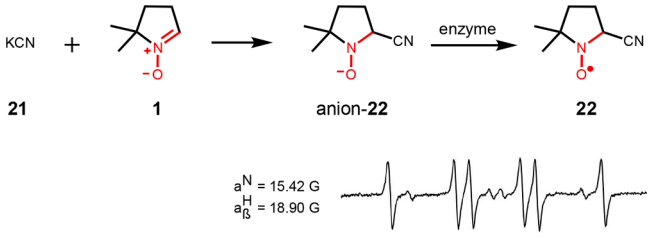
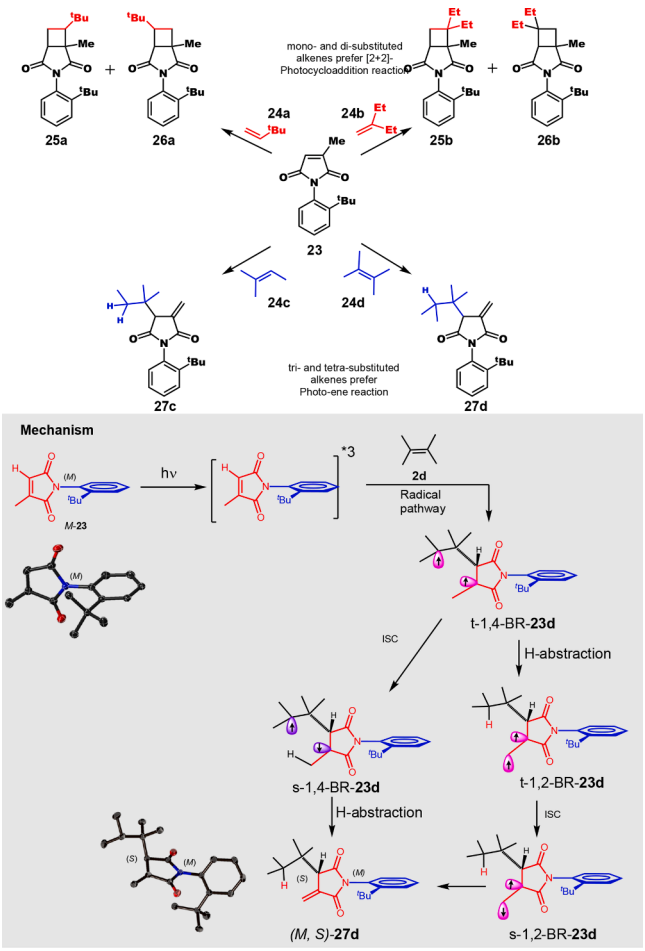


Fig. 7. EPR spectrum of DMPO/CN spin adduct 22 formed from the reaction of potassium cyanide 21 with DMPO 1. Adapted with permission from American Chemical Society (reference [25]).

30,32] Sivaguru and co-workers demonstrated how this approach can be extended to bimolecular reactions using a maleimide and alkene model system [27,33].

With mono or di-substituted alkenes **24a-b** maleimide **23** (Scheme 8) underwent [2 + 2] photocycloaddition leading to the cyclobutane products (products **27a-b**; Scheme 8-top). Conversely, photoreaction of

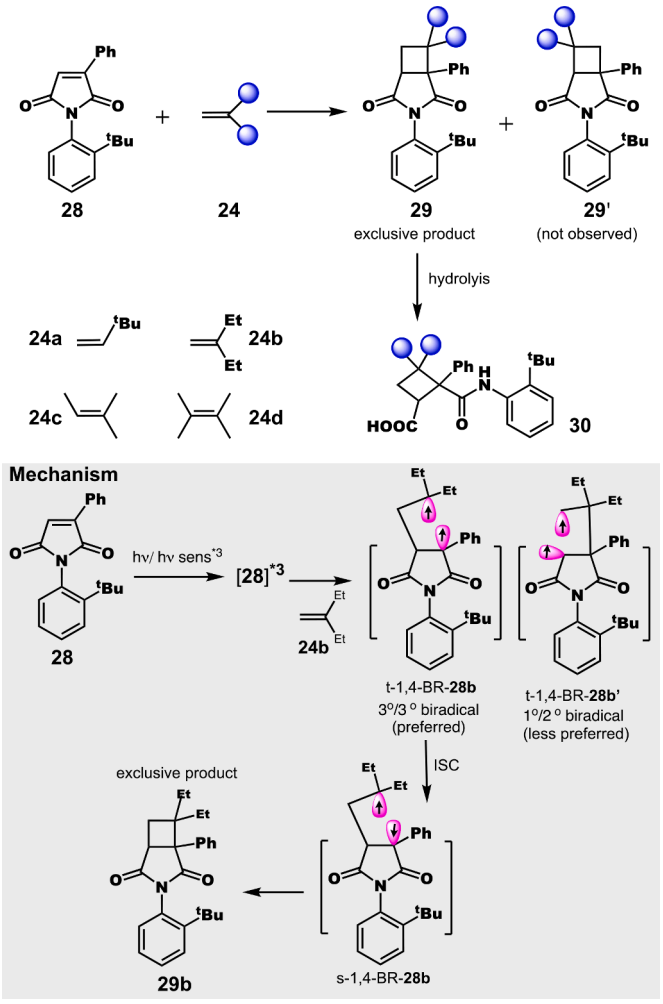


Scheme 8. Photoreactivity of maleimide with mono-, di-, tri-, and tetrasubstituted alkenes.

maleimide **23** with tri- and tetra-substituted **24c-d** led to photo-ene product (products **27c-d**; Scheme 8-bottom). By employing atropisomeric maleimide, enantioenriched photoproduct with >95% ee was observed. A mechanistic model for the photoreaction involved a triplet excited M-**23** that reacted with alkene **24d** to form triplet 1,4-biradical t-1,4-BR-**23d.**This triplet biradical abstracted the allylic hydrogen of in M-**23** through a cyclic 6-memembered transition state to form triplet 1,2-biradical t-1,2-BR-**2d,**followed by intersystem crossing and recombination to from the photo-ene product **27d**. It was postulated that the triplet 1,4-biradical intermediate reacted at a faster rate in mono and disubstituted alkenes as it featured a primary radical center leading to cyclobutane product. In tri- and tetra-substituted alkenes the triplet biradical formed during the course of the reaction featured a tertiary radical center that had a relatively longer lifetimes that abstracted the allylic hydrogen atom leading to the formation of the photo-ene product [27].

Extending the photo reactivity of maleimides, Sivaguru and coworkers also reported the regio-selective [2 + 2] photocycloaddition of atropoisomeric phenyl maleimides [33]. Energy transfer sensitization with thioxanthone led to triplet excited phenyl maleimide **28** that reacted with 1,1-disubstitued olefins **24** resulting in the exclusive formation of 1,2-disubsitued cyclobutane adduct **29**. By employing atropisomeric maleimides **28** enantioenriched photoproduct **29** was observed with excellent isolated yields (Scheme 9). Based on photophysical investigations it was proposed that the olefin **24** adds to a triplet excited maleimide to form a 1,4 triplet biradical which can undergo ring closure to form cyclobutane product **29** (Scheme 9).

Sonntag and co-workers(34) demonstrated that photo-excited



Scheme 9. Intermolecular 2 + 2 photocycloaddition of atropisomeric phenyl maleimides with olefins.

maleimide **31** underwent intersystem crossing into the triplet state **32** that can be quenched by three different mechanisms: a) hydrogen transfer to form maleimide-hydrogen adduct **35**; b) electron transfer to form radical anion **34**; and c) energy transfer to form ground state maleimide **33**. It was pointed out that unsaturated monomers react by fast electron transfer and that they dominate the primary step in self-initiating maleimide-vinyl ether based resins (Fig. 8) [34]. They used pulsed (Fourier transfer) EPR for their studies, which is similar to the TREPR experiment discussed in the introduction except that pulsed microwave radiation is used and electron spin echoes are detected as the external magnetic field is swept. Note that as in TREPR, the observed signals are spin polarized by CIDEP.

Due to the diverse reactivity of maleimides we were interested in understanding their reactivity by EPR spectroscopy. [35] Irradiation of phenyl maleimide **28** (0.005 M) at 355 nm in the presence of excess amount of DMPO (0.020 M) in benzene was investigated by EPR spectroscopy (Fig. 9) [36]. Based on the photochemical reactivity of **28**, the signal is likely due to the spin adduct (Fig. 9) formed via a photoinduced electron transfer (eT) involving triplet excited **28** and DMPO (similar to what was observed by Sonntag and co-workers(34 [37],).

4. Outlook on using spin probes to investigate excited state chemistry

Manipulating excited state photochemical reactivity often presents challenges due to the type of reactive species involved. When encountering highly reactive radical species, EPR spectroscopy can be judiciously employed for deciphering reactivity of excited states. Both SSEPR and TREPR provide a powerful toolbox for chemists to understand the photoreactivity of organic molecules. Coupled with spin-trapping methods, EPR spectroscopy can be utilized to understand chemical processes that will open up new avenues to develop and explore novel chemical reactivity.

5. Conclusions

This article has highlighted several unique aspects of electron paramagnetic resonance (EPR) spectroscopy to help decipher excited state organic reactivity. Employing this technique can be a powerful tool to gain insights on photochemical reactivity. We have showcased the diverse photochemical reactivity of maleimides as a model system. Further efforts are underway in our laboratories to exploit spin trapping as a strategy for deeper understanding of the structure, dynamics, and excited state reactivity of molecules and materials.

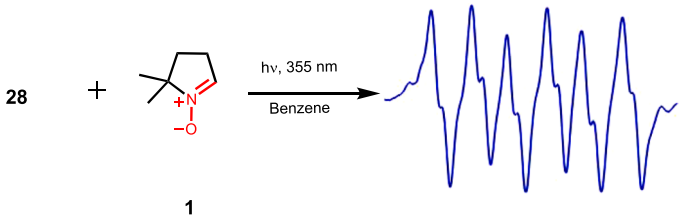


Fig. 9. EPR spectra upon irradiation of phenyl maleimide 28 in the presence of DMPO 1 at 355 nm in methanol.

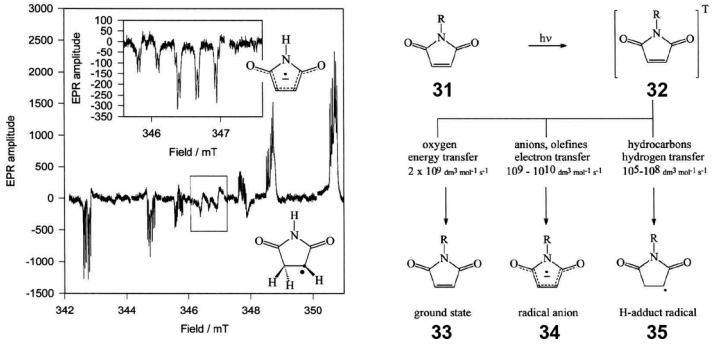


Fig. 8. (left) FT-EPR spectra of the maleimide radical anion and the maleimide hydrogen adduct; (right) Reaction scheme of triplet maleimide quenching. (Reproduced with permission from the Royal Society of Chemistry (reference [34]).

Author contributions

All authors equally contributed to the writing of the manuscript. The experiments were conducted by S.A.R. with guidance from M.D.E.F. and J.S.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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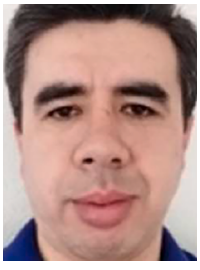

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