complex dependence of color on thermal history enhances the artistic possibilities of these cholesteric glasses.

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Photochemically Induced Dynamic Electron Spin Polarization. The 1,4-Naphthosemiquinone Radical in 2-Propanol

Sir:

Anomalous electron spin resonance emission spectra have been observed for a few free radicals in liquid systems produced by radiolysis,[1,2] by photolysis,[3,4] and by thermal reactions.[5] These relatively few observations, however, have generated a great deal of theoretical interests in recent years,[6–9] but the mechanisms of the dynamic electron polarization in various systems remain controversial. In the course of a systematic esr study of semiquinone radicals by flash photolysis and by the popular rotating sector techniques, we have unexpectedly observed esr emission from the photochemically produced 1,4-naphthosemiquinone radicals in liquid 2-propanol. We wish to report here these interesting experimental observations and to suggest a preliminary account for the dynamic electron polarization in this particular system.

Samples of degassed 2-propanol solution of 1,4-naphthoquinone were intermittently photolyzed within the cavity of a Varian 4502 esr 100-kc modulation spectrometer. The light source was an unfiltered 200-W super pressure Hg lamp which was coupled to a rotating disk capable of varying the dark-to-light ratio between 20 and 200 and the light period being as short as 200 μsec. Steady irradiation of the solution led to a well-resolved spectrum which is readily interpreted as due to the 1,4-naphthosemiquinone radicals. Under intermittent irradiation, the buildup and the decay curves of the esr signal at a constant magnetic field were obtained by thousands of sweeps using a Fabri-tek 1074 computer. A typical curve observed is shown in Figure 1.

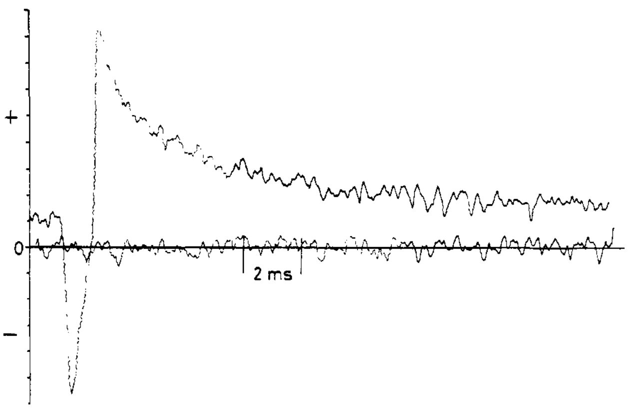

Figure 1. Time dependence of the esr signal intensity at constant magnetic field of the 1,4-naphthosemiquinone radicals in 2-propanol: absorption mode (+), emission mode (−).

Immediately after the light pulse the esr signal was in the form of emission which reverted to the normal absorption mode as the light pulse decayed with a time constant of about 300 μsec. The esr absorption further decayed according to a second-order kinetics due to self-reaction of the radicals. It was established that all hyperfine components of the radical exhibited the same behavior. Atkins and coworkers[3] have also observed similar phenomenon in the laser flash photolysis of some carbonyl compounds. However, in the present experiment using relatively much slower pulses from a rotating sector, it is rather surprising that emission could be observed.

We suggest that the chemically induced dynamic electron polarization (CIDEP) of the semiquinone radical in the present system is due to initially optically spin-polarized triplet states of the parent quinone, which subsequently abstract a hydrogen atom from the solvent 2-propanol with retention of the electron polarization. The phenomenon of optical spin polarization in organic triplet states is now fairly well established.[10–13] The following sequence of events is proposed to account for the experimental observation. The quinone is firstly excited by light to some higher singlet states which cross over to a triplet state. One might expect that the rates of the intersystem crossing from the excited singlet to the three sublevels of the lowest triplet state are not equal;[10,11] hence, it is possible that the upper sublevel, $|\alpha,\alpha\rangle$ is more populated than the lower sublevel $|\beta,\beta\rangle$. Further theoretical calculation will be performed to justify this polarization of the triplet 1,4-naphthoquinone molecules. If the hydrogen abstraction occurs before the triplet spin depolarization takes place by spin–lattice relaxation, the resultant semiquinone radical will be initially populated in a manner that is mainly determined by the triplet polarization; *i.e.*, $|\alpha,\alpha\rangle \rightarrow |\alpha,\alpha,\beta\rangle$ and $|\beta,\beta\rangle \rightarrow |\beta,\beta,\alpha\rangle$. This means that the spin polarization is retained in the semiquinone radical and esr emission is expected from all hyperfine components. This mechanism also predicts that the counter 2-propanol radical would give a totally emissive esr spectrum.

Selective population of triplet sublevels as a route to electron polarization has been considered by other authors but has been discarded on the grounds of a too long lifetime of the triplet state as compared to the spin–lattice relaxation times.[8,14] It should be pointed out here that spin–lattice relaxation times have not

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been experimentally measured for any organic triplet molecules in solution but they can only be estimated theoretically.[15,16] We also emphasize here that under favorable conditions, the hydrogen abstraction rate (the pseudo-first-order rate, not the rate constant) of the triplet molecules can be comparable or even greater than the spin-lattice relaxation rate. For example, it has recently been estimated for *p*-benzoquinone in the laser-flash photolysis that the rate of hydrogen abstraction from solvent ethanol is[17,18] probably greater than 10^8 sec^{-1}. Assuming the zero-field splitting of the n,π* triplet of 1,4-naphthoquinone is of the same order of magnitude of that of the n,π* triplet benzophenone,[19] the spin–lattice relaxation rate in the present system could be estimated theoretically[14,20] to be about 10^8 sec^{-1}. Since the hydrogen abstraction rate is several times greater in 2-propanol than in ethanol,[21] it is probable that in the present system the hydrogen abstraction rate is greater than the spin–lattice relaxation rate of the triplet. Furthermore, as the Boltzmann population difference of the two levels is only about 0.75% of the total population, the hydrogen abstraction rate could even be one order of magnitude smaller than the spin–lattice relaxation rate and it would still be possible for an emissive spectrum to be observed.

A brief comparison of our present interpretation and the elegant "radical-pair" theory[6–9] is now given. The radical-pair theory is originally developed for the CIDNP phenomenon and beautifully accounts for most of the CIDNP experiments. While the radical-pair theory holds great potential in explaining certain CIDEP experiments, it cannot be taken as a universal mechanism for *all* CIDEP phenomenon. At the same time we do not hint that our proposed mechanism is a general one, because radicals are produced in different manners in different systems. Nevertheless, the main difference between the present mechanism and the radical-pair theory is that the latter is independent of the previous history in the formation of radicals. Because of this fundamental difference, it is possible to design further experiments to distinguish between these two mechanisms. For example, the radical-pair theory predicts that it is possible to observe anomalous population of the spin levels of radicals with uncorrelated spins.[9] However, there are many stable radicals[22] observed independent of the history of their formation and none has been reported to lead to anomalous population of the spin levels. Also according to the radical-pair theory, the radical pair should possess opposite polarization, whereas our proposed mechanism predicts the same polarization for the counter radical. A formal development of our proposed theory will be reported in a forthcoming paper.

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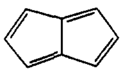
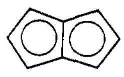
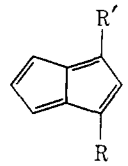
A Stable Transition Metal π Complex of Dimethylaminopentalene

Sir:

Pentalene (**1**), the lower homolog of naphthalene, has been the subject of considerable interest and controversy to both synthetic and theoretical chemists since 1922 when Armit and Robinson first suggested that this unique molecule might possess aromatic character.[1] Recent theoretical calculations are at odds with this early suggestion and predict that the singlet ground state of pentalene should be antiaromatic and possess the polyolefin structure **1a** rather than the delocalized structure **1b**.[2] Forbidden and allowed transitions in the uv region, bond distances, the heat of formation, and the ionization potential have all been calculated for the pentalene molecule.[2]


1a


1b


2a, R = R′ = $(CH_3)_2N$
b, R = CH_3; R′ = H

Unfortunately, experimental verification of these predictions has not been obtained since all attempts to prepare pentalene have met with failure.[3] Hexaphenyl-[4] and bis-1,3-dimethylaminopentalene (**2a**)[5] have been synthesized and shown to be relatively stable entities. In contrast, evidence supporting the existence of 1-methylpentalene (**2b**) could only be obtained by generating the molecule at −196° and determining its uv and ir spectra at the same temperature.[6] Dimerization of **2b** occurs rapidly above −100°.[6] Pentalene itself is also expected to be highly reactive and exhibit properties similar to **2b**.

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