

EXTERNAL MAGNETIC FIELD DEPENDENT INFLUENCE OF LANTHANIDE IONS ON THE CHEMISTRY OF RADICAL PAIRS IN MICELLES

Nicholas J TURRO, Xuegong LEI, Ian R GOULD and Matthew B ZIMM

Department of Chemistry, Columbia University, New York, NY 10027, USA

Received 24 June 1985 in final form 22 July 1985

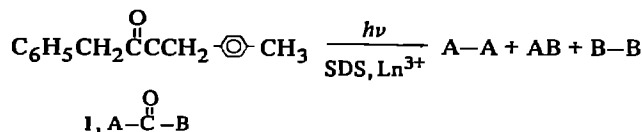
The behavior of geminate triplet benzyl radical pairs in anionic micelles has been investigated as a function of added lanthanide ions (Ln^{3+}) in the presence and absence of a laboratory field. Although the percent of geminate radical coupling is insensitive to the nature of added Ln^{3+} in the absence of a laboratory field (except for a salt effect) in the presence of a laboratory field the percent cage is significantly affected by paramagnetic Ln^{3+} ions but not by diamagnetic Ln^{3+} ions or by Eu^{3+} .

The effect of trivalent lanthanide ions (Ln^{3+}) on the decay of naphthoquinone ($\dot{\text{N}}\text{QH}$) detergent ($\dot{\text{R}}$) radical pairs produced by photolysis of 1,4-naphthoquinone (NQ) in sodium dodecyl sulfate (SDS) micelles has been shown by Sakaguchi and Hayashi [1] to depend on the number of unpaired electron spins of Ln^{3+} associated with an SDS micelle. However, the Ln^{3+} are effective in accelerating the decay of NQH/ $\dot{\text{R}}$ radical pairs only in the presence of an external laboratory field. A long-lived component of the decay that was not influenced by Ln^{3+} in the presence or absence of a laboratory field was assigned to $\dot{\text{N}}\text{QH}$ radicals that escaped from SDS micelles. The variation of products of reactions of NQH/ $\dot{\text{R}}$ radical pairs and their dependence on laboratory fields and on Ln^{3+} was not reported [1]. The firm establishment of the influence of Ln^{3+} and laboratory fields on product structures is important because the mechanistic origin of the long decay of radical pairs in micellar systems is still a matter of current research [2]. We report the influence of Ln^{3+} on the products of the photolysis of dibenzyl ketone (DBK) in SDS micelles, in the presence and absence of Ln^{3+} and of a laboratory field (scheme 1).

Our results confirm the conclusions of the time resolved experiments of Sakaguchi and Hayashi [1], and reveal a surprise for the behavior of Eu^{3+} , an ion that had not been reported in their investigation.

The percent cage was determined as described previously [3] from the ratio of radical coupling products AA, AB and BB. In all cases* mass balances were >95%. The cage effect (fig. 1a) undergoes a modest increase (attributed to a salt effect on micelle structure) when Ln^{3+} is added to aqueous solutions containing sodium dodecyl sulfate (SDS) micelles and 1 in the earth's magnetic field. Although the influence of La^{3+} , Lu^{3+} and Gd^{3+} are similar (the percent cage increasing from $\approx 36\%$ to $\approx 45\%$ as the $[\text{Ln}^{3+}]$ is increased from 0 M to 10 mM), a dramatic difference in the influence of La^{3+} or Lu^{3+} relative to Gd^{3+} is observed when the photolysis of 1 in SDS micellar solution is conduct-

* The concentration of SDS was 70 mM in all reported experiments. Qualitatively similar results of the internal magnetic field effect were obtained for photolysis of benzyl esters and benzyl sulfones in SDS micelles, thereby ruling out a special effect for ketones.



Scheme 1

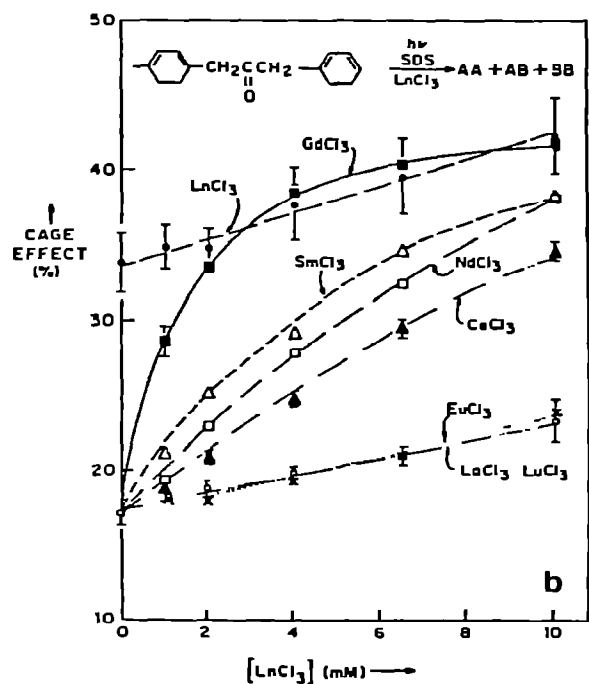
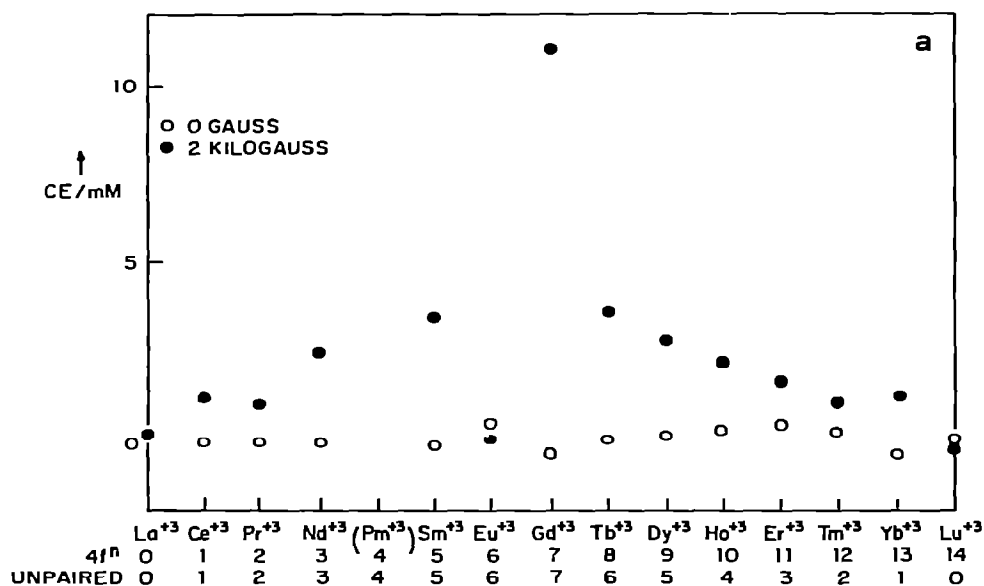


Fig 1 (a) Plot of the initial slopes of insert (b) versus Ln³⁺. Listed under each Ln³⁺ is the number of 4f electrons possessed by the ion and the number of unpaired 4f electrons. Pm³⁺ was unavailable for testing and is included for completeness of the family. (b) Cage effect for photolysis of 1 in SDS micellar solutions as function of added lanthanide ions. [SDS] = 70 mM. The line labeled LnCl₃ refers to the results obtained for each lanthanide at 0 G, all other lines refer to experiments performed at 2000 G.

ed in a magnetic field of 2000 G (fig 1b) In the latter case addition of La^{3+} or Lu^{3+} causes a small increase in the percent cage from $\approx 19\%$ to $\approx 24\%$ at 0 M and 10 mM, respectively, whereas addition of Gd^{3+} causes an increase in the percent cage from $\approx 19\%$ to $\approx 40\%$ at 0 M and 10 mM, respectively Addition of other lanthanides results in the family of curves shown in fig 1a. At 0 G, the family of curves is experimentally indistinguishable, but at 2000 G the curves become distinct for all of the lanthanides except La^{3+} , Lu^{3+} and Eu^{3+} which induce only small changes comparable to those expected for salt effects

The initial portion of each curve (up to ≈ 2 mM) is essentially linear The slopes of this linear region represent the sensitivity of the cage effect to added lanthanide A plot of the initial slopes versus the number of f electrons is shown in fig. 1a.

The origin of the effects of lanthanide ions on the behavior of benzyl radical pairs may be sought in changes in the structure and nature of the micellar environment brought about by the Ln^{3+} ions or in changes in the dynamics of the triplet radical pairs brought about by the magnetic characteristics of the Ln^{3+} ions. La^{3+} is the lightest and largest ion, whereas Lu^{3+} is the heaviest and smallest ion of the Ln^{3+} series investigated Both La^{3+} and Lu^{3+} are diamagnetic The observation of nearly identical behavior of La^{3+} and Lu^{3+} at 0 G and at 2000 G argues strongly that the entire series of Ln^{3+} ions behave similarly (as simple salts) with respect to their influence on micellar structures

The lanthanide effect on the percent cage is, therefore, attributed to an "internal magnetic field" effect of the paramagnetic ions** as proposed by Sakaguchi and Hayashi [1], i.e. the effect scales as the number of electron spins with the exception of Eu^{3+} The unique status of Eu^{3+} , which possesses six unpaired electrons, may be attributed to the fact that this ion is diamagnetic in its ground electronic state because of a fortuitous cancellation of spin and orbital magnetic moments [4] A mechanism consistent with our results is shown in fig. 2, and is related to proposals [1,5] of an internal magnetic field induced relaxation of the triplet sublevels of a radical pair (^3RP). At 0 G the three triplet sublevels (T_+ , T_- , and T_0) are all strongly mixed by the rapid rotational motions of the radical fragments Intersystem crossing from the strongly mixed state to the singlet pair (^1RP) occurs efficiently. The magnitude of the cage effect reflects the

** Interestingly, the slopes plotted in fig 1a are nearly proportional to $S(S+1)$, where S is the electron spin quantum number of the rare earth ion This is an intriguing observation, since for the lanthanides J , and not S , is expected to be the pertinent quantum number The magnetic moments of the ions are expected to be related to $g^2J(J+1)$, where g is the Landé g -factor. We cannot deduce a correlation between the slopes of fig 1a and the magnetic moments of the ions If crystal field interactions were sufficient to quench the ions orbital momentum, S would become a pertinent quantum number Such a situation is, however, unknown for the lanthanide ions

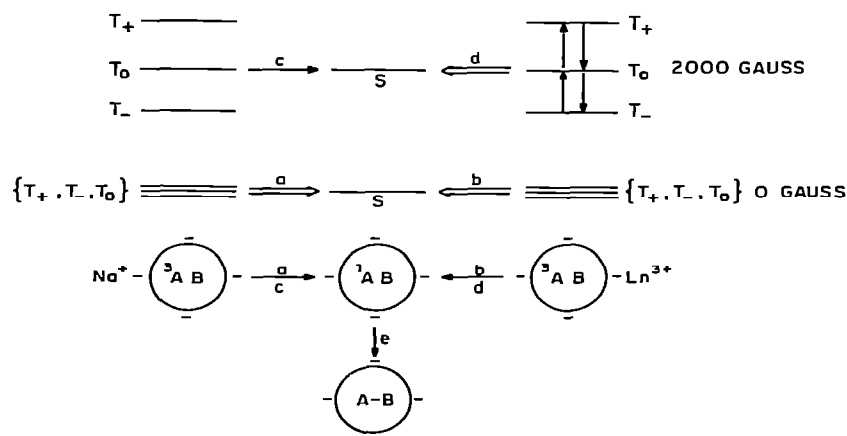


Fig 2 Proposed mechanism for the magnetic field effect on the influence of Ln^{3+} ions on the behavior of geminate radical pairs

competition between ISC to ^1RP and escape processes available to ^3RP . At 2000 G the T_+ and T_- states of ^3RP are split in energy from T_0 . Thus, in a field of 2000 G only $T_0 \rightarrow ^1\text{RP}$ ISC is efficient. As a result, escape processes for T_+ and T_- compete more efficiently with ISC to ^1RP and the percent cage decreases. It is postulated that the internal magnetic field of the Ln^{3+} ions "reverses" the effect of the external field by causing relaxation of the T_+ and T_- states to the T_0 and S states. When this occurs, all three sublevels can enjoy efficient ISC to ^1RP and, hence, a higher cage effect results. Mechanisms involving sublevel relaxation may become important when a third source of electronic magnetic spin interacts with the electronic spins of a radical pair. Micelles may be employed to enhance such effects by both providing a microscopic reaction space or super cage which generally enhances the magnitude of magnetic effects and by binding together the radical pair and the species responsible for inducing relaxation.

The authors thank the National Science Foundation and the American Cyanamid Company for their generous support of this research. MBZ thanks the NSF for a predoctoral fellowship.

References

- [1] Y. Sakaguchi and H. Hayashi, *Chem. Phys. Letters* 106 (1984) 420, H. Hayashi and S. Nagakura, *Bull. Chem. Soc. Japan* 57 (1984) 322; Y. Sakaguchi and H. Hayashi, *J. Phys. Chem.* 88 (1984) 1437.
- [2] J. C. Scaiano and E. B. Abuin, *Chem. Phys. Letters* 81 (1981) 209, J. C. Scaiano, E. B. Abuin and L. C. Stewart, *J. Am. Chem. Soc.* 104 (1982) 5673.
- [3] N. J. Turro and G. C. Weed, *J. Am. Chem. Soc.* 105 (1983) 1981.
- [4] S. P. Sinha, *Complexes of the rare earths* (Pergamon Press, Oxford, 1966), W. de W. Horrocks and M. Albin, *Progr. Inorg. Chem.* 31 (1984) 1.
- [5] T. Ulrich and U. E. Steiner, *Chem. Phys. Letters* 112 (1984) 365.