J. Am. Chem. Soc. **1998,** *120,* 8521−8522 8521

Intrazeolite Photochemistry. 24. Enantioselective Discrimination in the Quenching of Chiral Mn(II)salen Complexes Encapsulated inside Y Zeolite by Chiral 2-Butanols

María J. Sabater,[†] Sara García,[†] Mercedes Alvaro,[†]
Hermenegildo García,*[,†] and J. C. Scaiano*[,‡]

Instituto de Tecnología Química y Departamento de Química
Universidad Politécnica de Valencia, Apartado 22012
46071 Valencia, Spain
Department of Chemistry, University of Ottawa
Ottawa K1N 6N5, Canada

Received April 20, 1998

Enantioselective catalysis is the most powerful methodology in asymmetric synthesis.[1] A question of paramount importance is how to evaluate the degree of intrinsic enantioselective discrimination of the activated complex formed by the chiral catalytic site interacting with the substrate. A direct approach would require a fast kinetic technique capable of monitoring the site−substrate interaction. Enantioselective catalysts related to our work are Mn(III)salen complexes that are exceedingly good catalysts for the asymmetric epoxidation of alkenes.[2,3]

To improve the catalytic asymmetric induction it is necessary to favor the interaction of the substrate with the chiral center. One promising strategy is to conduct the reaction in a restricted reaction cavity.[4] Thus, confinement of the active complex inside a microporous solid may enhance the chirality transfer by forcing the substrate to be arranged in the appropriate geometry around the catalytic site.

In the present communication, we report that excited states of chiral Mn(II)salen complexes [salen = 1,2-bis(salicylideneimino)-cyclohexane] encapsulated inside the Y supercages are stereoselectively quenched by enantiomerically pure 2-butanols. There are two major contributions in this work: first, we find that time-resolved diffuse-reflectance (DR) spectroscopy is a convenient tool to monitor directly the enantioselective discrimination of a chiral quencher. Second, the zeolite matrix contributes positively to the process in two ways: (i) by stabilizing the unstable Mn(II) complex and (ii) by enhancing the enantioselective complex−quencher interaction. No such time-resolved techniques have ever been applied to the determine the enantiomeric discrimination within zeolites.

Preparation of Mn(II)salen complexes embedded in zeolite Y was accomplished by synthesizing the ligand from salicylaldehyde and 1,2-diaminecyclohexane (either *R,R* or *S,S*) around resident Mn^{2+} ions previously introduced by ion exchange (Scheme 1). The resulting Mn(II)salen-Y samples contain an average of one Mn(II) every five supercages, and the Mn^{2+}/salen ratio based on chemical analysis was 0.8. Characterization of the Mn(II)salen-Y zeolites was accomplished by DR, IR, and EPR spectroscopies.

When embedded within the zeolite supercages, Mn(II)salen complexes are stable for several months. This behavior sharply contrasts with that of the same Mn(II)salen complex in acetonitrile solution. Although the Mn(II)salen complex has been reported in solution, it has been found to undergo a spontaneous oxidation to the more stable Mn(III)salen complex.[5] The change in the Mn oxidation state can be easily followed by absorption spectroscopy.

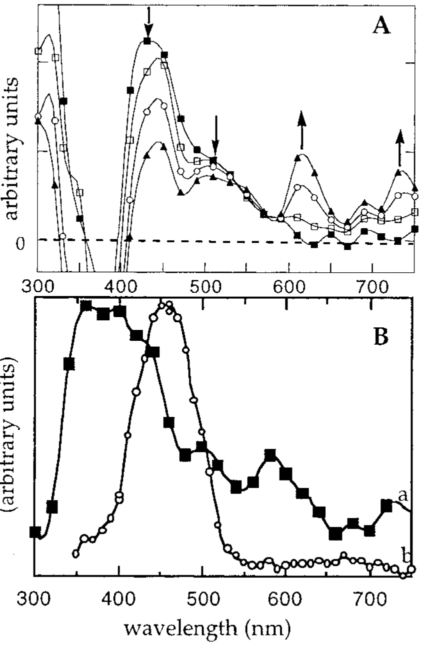
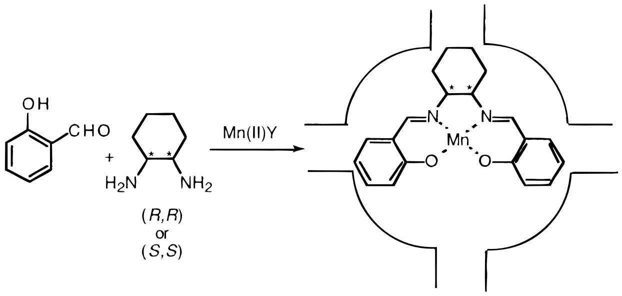


Figure 1. Time-resolved DR (A) or absorption (B) spectra upon 266-nm excitation of N_2-purged samples. (A) (*S,S*)-Mn(II)salen-Y recorded 5 (■), 15 (□), 25 (○), and 40 (▲) μs after 266-nm excitation. The arrows indicate the decay and growth of the bands. (B) (*S,S*)-Mn(III)salen complex (plot a, ■) and the (*S,S*)-salen ligand (plot b, ○) in acetonitrile (10^{-4} M in both cases) recorded at 1 and 72 μs, respectively.

Scheme 1



The transient DR spectra of (*S,S*)-Mn(II)salen-Y recorded at different times after the laser flash are shown in Figure 1A. They show two absorption bands at 440 and 515 nm decaying with the same kinetics and two other absorptions at 615 and 740 nm growing simultaneously with an isosbestic point at ~540 nm. The decay of the first transient and the growth of the second one were concurrent. This indicates that there is an interconversion where the decaying transient is the precursor of the growing in. The corresponding *R,R* enantiomer exhibits the same spectrum and kinetics of transient interconversion within the resolution limit of the DR technique, as expected. The luminescence of related Mn(II)−bipyridine complexes has been rationalized as emission from a long-lived sextet Mn(III)−ligand$^{\bullet-}$ charge transfer (^{6}CT) populated from an initial ^{4}CT Mn(III)−ligand$^{\bullet-}$ excited state.[6]

[†] Universidad Politécnica de Valencia.

[‡] University of Ottawa.

(1) Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, 1983.

(2) Jacobsen, E. N.; Zhang, W.; Güller, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703.

(3) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063.

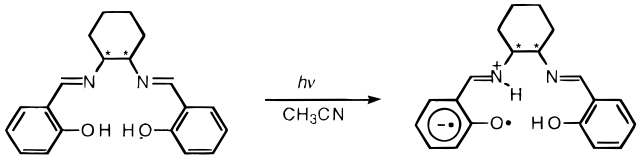
(4) Sabater, M. J.; Corma, A.; Domenech, A.; Fornés, V.; García, H. *Chem. Commun.* **1997**, 1285−1286.

(5) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309−2320.

(6) Knops-Gerrits, P.-P. H. J. M.; De Schryver, F. C.; van der Auweraer, M.; van Mingroot, H.; Li, X.-y.; Jacobs, P. A. *Chem. Eur. J.* **1996**, *2*, 592−597.

S0002-7863(98)01326-2 CCC: $15.00

Scheme 2



This is consistent with the transients observed here by time-resolved DR. Observation of long-lived emission ($\tau \approx 10$ ms) in our chiral Mn(II)salen complexes strongly supports this rationalization.

We attempted to obtain the transient spectrum of the Mn(II)-salen complex in acetonitrile solutions. With this objective in mind, $Mn(AcO)_2$ was added to a solution of the salen ligand in CH_3CN/H_2O. However, as indicated earlier, the tendency of Mn(II)salen to undergo oxidation in solution is so high that, in our hands, unavoidable trace amounts of molecular oxygen were sufficient to cause the Mn(II) to Mn(III) oxidation even under the most careful workup of the diluted, nitrogen-purged samples required for the LFP experiments.[7] Therefore, it is not surprising that, instead of a spectrum analogous to that found for the Mn(II)salen-Y sample, the transient spectrum in solution was coincident to that obtained when submitting to photolysis a $Mn(III)salen^+$ complex (Figure 1B). This failure to obtain the transient spectrum of Mn(II)salen in solution reveals the important role played by the zeolite solid matrix that provides a convenient cavity to stabilize this elusive species.

Since the chiral environment is provided by the ligand, we also examined the LFP of salen in CH_3CN. The transient spectrum of salen is characterized by a single absorption band at 455 nm (Figure 1B) with a first-order decay (2.6 ms lifetime) and quenched by H_2O (k_q 2.05×10^3 M^{-1} s^{-1}) and cyclohexadiene (k_q 8.05×10^4 M^{-1} s^{-1}), but not by oxygen. The spectrum and the chemical reactivity is compatible with a zwitterionic immonium phenoxide arising by intramolecular proton transfer from the phenolic moiety to the Schiff base (Scheme 2).

Quenching experiments using enantiomerically pure (*R*)- and (*S*)-2-butanol were carried out for the Mn(II)salen-Y powders and compared to those of the quenching of the salen ligand in solution. Adsorption of the butanols into Mn(II)salen-Y was accomplished by connecting the zeolite cell with a reservoir of the appropriate butanol enantiomer at 50 °C for increasing periods of time. The amount of butanol adsorbed was calculated by combustion chemical analysis and varied from 0 to 2.3 molecules of butanol per supercage as average in the bulk solid. It was observed that, for (*S,S*)-Mn(II)salen-Y, (*S*)-2-butanol is a dynamic quencher of the initial ^4CT transient, the kinetics of disappearance being faster as the average of (*S*)-2-butanol per supercage increases (Figure 2A). In addition to the influence on the kinetics (dynamic quenching), (*S*)-2-butanol also produces a progressive decrease of the initial signal intensity (static quenching). At the maximum loading, $k_0 + k_q^{SS+S}$ was 1.54×10^5 s^{-1} (calculated by the best fit to a single monoexponential decay). This behavior of (*S*)-2-butanol contrasts with that for the *R* enantiomer (Figure 2B). Under identical conditions, (*R*)-butanol does not affect appreciably the (*S,S*)-Mn(II)salen-Y transient decay ($k_0 + k_q^{SS+R} \approx k_0 = 1.14 \times 10^4$ s^{-1}).

To further confirm that the different quenching by (*R*)- and (*S*)-butanols is due to chiral discrimination, the same experiments were carried out with (*R,R*)-Mn(II)salen-Y. Exactly the reverse situation was observed, the transient of (*R,R*)-Mn(II)salen-Y being quenched by (*R*)-2-butanol but not affected by the *S* enantiomer. This is conclusive evidence that the origin of the quenching differences between (*R*)- and (*S*)-butanols is chiral recognition.

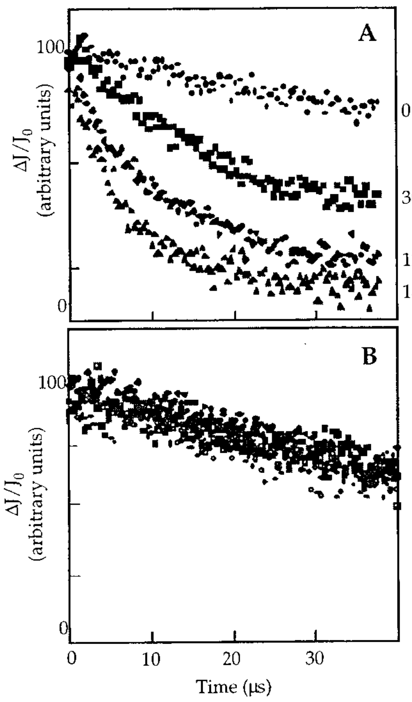


Figure 2. Normalized transient decays monitored at 440 nm after 266-nm excitation of (*S,S*)-Mn(II)salen-Y complex upon contacting at 50 °C the powder with 2-butanol vapors for 0 (●), 30 (■), 120 (▼), and 180 (▲) min, corresponding to averages of 0, 0.5, 1.7, and 2.3 butanol molecules per zeolite supercage, respectively. (A) (*S*)-2-Butanol. (B) (*R*)-2-Butanol.

The transients generated upon laser excitation of the (*R,R*)- and (*S,S*)-salen ligands are also quenched differently by (*R*)- and (*S*)-2-butanol, although the magnitude of the effect was notably smaller. Thus, the *S,S* ligand in solution is quenched by (*S*)-2-butanol with a quenching constant ($k_q^{SS+S} = 9.3 \times 10^4$ M^{-1} s^{-1}) higher than that obtained for (*R*)-2-butanol ($k_q^{SS+R} = 4.1 \times 10^4$ M^{-1} s^{-1}). The opposite applies for the *R,R* ligand for which identical k_q values were obtained for the reverse enantiomers. The k_q^{SS+S}/k_q^{SS+R} quenching ratio for the ligand is, then, about 2, while for the Mn(II)salen-Y complex at the maximum butanol loading, the ratio k_q^{SS+S}/k_q^{SS+R} is ≥ 20. This comparison suggests that the zeolite host favors the enantioselective discrimination by providing a restricted reaction cavity.

In summary, time-resolved DR has proven a convenient spectroscopic tool to probe the enantioselective quenching of the ^4CT transients generated in the LFP of Mn(II)salen complexes encapsulated inside Y zeolite by chiral 2-butanols. Direct comparison of the degree of enantiodiscrimination for the same complexes in solution is not possible owing to their tendency to undergo spontaneous oxidation to Mn(III)salen complexes. In any case, the level of enantiodiscrimination on the Mn(II)salen-Y complex is much higher than that measured for the salen ligand in solution.

Acknowledgment. Financial support by the Spanish DGICYT (H.G., Grant MAT97-1016-CO2) and the Natural Science and Engineering Research Council of Canada (J.C.S.) through an operating grant is gratefully acknowledged. M.J.S. and S.G. thank the DGICYT for a reincorporation fellowship and a postgraduate scholarship, respectively. We are indebted with Mr. A. Simard for his skillful help in the laser experiments.

JA981326Z

---

(7) Laser experiments were performed at concentrations in the 10^{-4} M range, making the total exclusion of traces of oxygen more difficult than in the case of organic reactions, where a small amount of substrate may play a sacrificial role in depleting residual oxygen. A comparable "sacrificial" concentration in our experiments leads to a significant destruction of the substrate.