THE EFFECT OF MEDIUM ON CIDNP KINETICS IN GEMINATE RECOMBINATION OF BIRADICALS. EXPERIMENT AND CALCULATION


Institute of Chemical Kinetics and Combustion and
International Tomographic Centre
Novosibirsk, 630090, Institutskaia str. 3, Russia

(Received 24 April 1992; accepted 30 April 1992)

ABSTRACT

Submicrosecond flash-CIDNP was used to study the dependences of the kinetics and amplitude of CIDNP, arising in biradicals produced in the photolysis of cyclic aliphatic ketones on the temperature and viscosity of the medium. It has been found that for biradicals the geminate CIDNP increases with the diffusion coefficient of the medium. The theoretical consideration of geminate recombination kinetics is based on the numerical solution of the stochastic Liouville equation for the Fourier transform of the spin density matrix. The dependences of nuclear polarization on the lifetime of the triplet state of initial ketone, on electronic paramagnetic relaxation times, on scavenging rate, and on exchange interaction have been analyzed and compared with experimental data. The conditions of quantum beats manifestation in CIDNP kinetics have been considered theoretically.
INTRODUCTION

The influence of molecular and spin dynamics on geminate evolution of spin-correlated radical pairs (RP) is one of the principal problems in studying magnetic and spin effects in chemical reactions. This influence manifests itself most clearly in electronic and nuclear spin polarizations (CIDEP and CIDNP) whose values are strongly dependent on the mechanism of molecular dynamics [1]. In normal RP, the geminate recombination competes with the escape into the bulk followed by participation of radicals in homogeneous processes. In nonviscous media, the time between re-encounters of RP partners is small compared to the time of S-T conversion and, hence, the increased viscosity should lead to the increased amplitude of spin polarization in geminate processes [1]. For CIDNP, this has been experimentally demonstrated in a study on the dependence of nuclear polarization in geminate RP recombination on the diffusion coefficient of the medium [2].

The problems of molecular and spin dynamics of restricted-diffusion RP (biradicals, RP in micelles and zeolites, etc.) have recently received increased attention. Biradicals can arise as a result of bond cleavage in cyclic molecules or as a result of intramolecular electron (or proton) transfer and contain two radical centers linked by flexible polymethylene chain. A characteristic feature of biradicals is the absence of irreversible diffusive separation of the radical centers, hence the geminate recombination and disproportionation are the only channels of biradical decay. It has been shown [3-8] that for chains with 10-12 segments under normal conditions the conformational motion of polymethylene chain is fast, and the spin dynamics is the limiting step for biradical lifetime. Thus, the biradical lifetime almost does not change with the diffusion coefficient. An increased diffusion coefficient leads to decreased time between re-encounters of radical centers; the number of re-encounters however increases, and hence one cannot predict the character of the diffusion coefficient dependence of CIDNP amplitude.

An important characteristic feature of biradicals is that the maximum separation of radical centers is limited by chain length. This accounts for the considerable exchange interaction of unpaired electrons, modulated by relative motion of radical centers. The exchange interaction has a significant influence on biradical decay kinetics and nuclear polarization formation in the products of biradical transformations. Temperature variations affect not only the rate of conformational motion of the biradical polymethylene chain, but also the biradical end-to-end distance distribution function [9-10] and, hence, the effective exchange interaction. Thus, the