A ^{31}P CIDNP Study of the Reactions of Dithiophosphate Metal Complexes at Various Magnetic Fields

Rafinad M. Gainullin,[a] Akhat V. Il'yasov*[a] and Kev M. Salikhov[b]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420083 Kazan, Tatarstan, Russian Federation. Fax: +7 8432 752253*
[b] *E. K. Zavoisky Physical-Technical Institute, Russian Academy of Sciences, 420029 Kazan, Tatarstan, Russian Federation. Fax: +7 8432 765075*

The reactions of dithiophosphate metal complexes of zinc(II), nickel(II), copper(II) and molybdenum(VI) with cumene and *tert*-butyl hydroperoxides have been investigated by ^{31}P CIDNP and the reaction rate constants determined; information about the spin dynamics of the radical pair has been obtained.

The antioxidant affinities of the zinc dithiophosphates are the subject of great research interest. However, to date it has been difficult to draw conclusions about the mechanism of the antioxidant reactions of such complexes, in particular, the first step of the chemical interactions. The creation of nuclear polarization (CIDNP) during free radical reactions offers new possibilities in establishing the nature and kinetics of the processes. Our preliminary studies of some phosphorus-containing metal complex reactions with hydroperoxides based on ^{31}P CIDNP experiments were described earlier.[1,2] We now expand into a study of dithiophosphate complexes of transition metals of zinc(II), nickel(II), copper(II) and molybdenum(VI) during their thermal decomposition in the presence of cumene and *tert*-butyl hydroperoxide. The reaction was carried out directly in the probe head of a CPX-100 "Bruker" NMR spectrometer ($H_0 = 2.15$ T, $\nu_p = 36.47$ MHz). Chlorobenzene as a solvent was purified according to a standard method.[3] The cumene and *tert*-butyl hydroperoxides were purified to 99.9% and 96%, respectively.[4,5] The experiments at low-field ($H_0 \sim 50$ mT) were carried out outside the probe head and the reaction product was then transferred to the recording spectrometer. We used a home-made temperature unit for temperature control in the low-field magnet.[6] It was established from an analysis of the polarized ^{31}P NMR signal of the reaction products that the peroxide radical forming interacts with a metal–ligand bond resulting in S–M–S cleavage and the subsequent removal of the sulfur atom (Fig. 1).

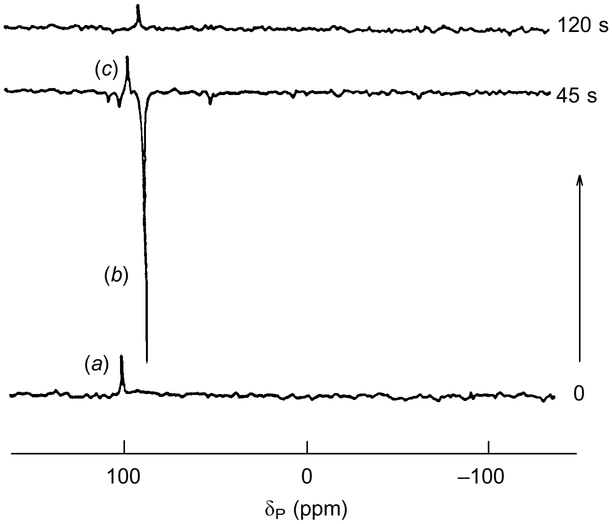
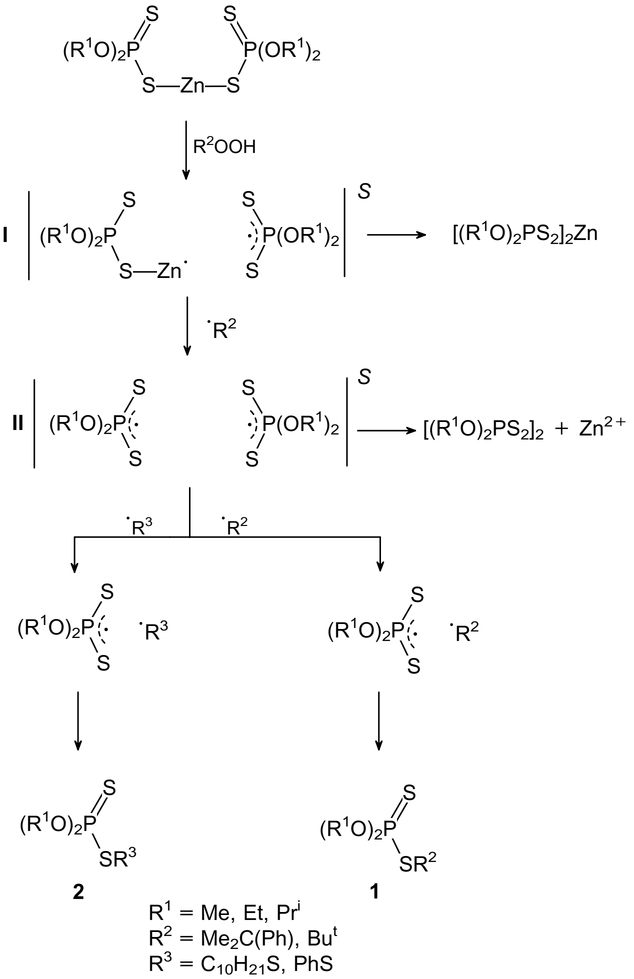


Fig. 1 ^{31}P NMR spectra of the reaction of zinc(II) dithiophosphate with cumene hydroperoxide in chlorobenzene at 343 K. (*a*), $[(EtO)_2P(S)S]_2Zn$; (*b*), $[(EtO)_2P(S)S]_2$; (*c*), $(EtO)_2P(S)OR^3$.

The spectra were recorded in 15 s intervals after mixing of the reagents in the NMR spectrometer probe head. The spectrum showed abnormal NMR emission (emm.) and absorption (abs.) signals beginning 45 s after mixing of the reagents. The analysis of the polarization pattern resulted in Scheme 1 for the chemical transformation.



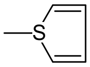
Scheme 1 The reaction of zinc(II) dithiophosphate with cumene hydroperoxide.

It is clear that the observed emission signal of the final product cannot be assigned to an S–T$_0$ transition in the radical pair **II** since the *g*-factor difference is 0 ($g \neq 0$). Apparently, the initial polarization is created in radical pair **I** for which $g = 0$, and is then transferred to **II** (memory effect) and to the bis(O,O'-dialkyldithiophosphoryl)disulfide. These results were confirmed by an investigation of the reactions at various magnetic field strengths. The addition of free radical acceptors (decanethiol, thiophenol) does not result in decreasing intensity of the polarized signal of bis(O,O'-dialkyldithiophosphoryl)disulfide. It is evident that polarization is created in cage polarization, with a change in the product arising in diffusion radical pairs only. For example, in the reaction of zinc dithiophosphate with cumene hydroperoxide a signal with $\delta_P = 93$ ppm (abs.) **1** was observed, but in the presence of decanethiol a product with $\delta_P = 90$ ppm (emm.) **2** was formed. The change in the sign

Table 1 The reaction rate constants for zinc(II) dithiophosphate with cumene hydroperoxide.

Compound	Rate constants $k/10^2\ \mathrm{s}^{-1}$
$[(\mathrm{EtO})_2\mathrm{PS}_2]_2\mathrm{Zn}$	2.2
$[(\mathrm{Pr^iO})_2\mathrm{PS}_2]_2\mathrm{Zn}$	2.7
$[(\mathrm{Bu^iO})_2\mathrm{PS}_2]_2\mathrm{Zn}$	3.1
$[(\mathrm{EtO})\mathrm{PS}_2(\mathrm{Th})]_2\mathrm{Zn}^a$	4.2
$[(\mathrm{C}_5\mathrm{H}_{11}\mathrm{O})\mathrm{PS}_2(\mathrm{Th})]_2\mathrm{Zn}^a$	4.3
$[(\mathrm{C}_6\mathrm{H}_{13}\mathrm{O})_2\mathrm{PS}_2]_2\mathrm{Zn}$	5.5
$[(\mathrm{Pr^iO})\mathrm{PS}_2(\mathrm{OC}_6\mathrm{H}_{13})]_2\mathrm{Zn}$	5.7

[a] Th =



of polarization can be explained using Kaptein's rules. For $g = 2.026$[7] which is larger than the g-factor of dialkoxydithiophosphoryl radicals, $g = 2.0189$.[8]

The antioxidant affinities of transition metal dialkyldithiophosphonates are connected with the sulfur-containing fragments of these molecules. However, up to now it has been difficult to draw conclusions about the influence of the phosphorus atom environment on the properties of these fragments. The concept of a correlation between structure and reaction ability is the basis for understanding both the reaction mechanism and the features of selective synthesis of certain compounds.

The investigation of dithiophosphates showed that the reaction rate constant dependence on substituent increases in the sequence $\mathrm{EtO} < \mathrm{Pr^iO} < \mathrm{Bu^iO}$ (Table 1). The trend of these results may be used as a basis for selective synthesis of certain compounds with antioxidant properties. CIDNP study of these reactions reveals an express method for determination of reaction rate constants without complicated calculations. The procedure for the measurement of reaction rate constants is described in ref. 1. Carrying out the reaction at different magnetic field strengths from 50 mT to 5.8 T has shown that the sign of polarization of bis(O,O'-dialkyldithiophosphoryl)disulfide does not change (Fig. 2). The polarisation behaviour is explained by the weak exchange interaction of the radicals inside the radical pair and it is necessary to account for the S–T_0 as well as S–T_+ and S–T_- transitions.

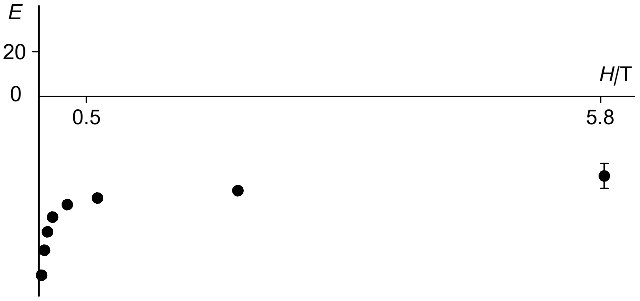


Fig. 2 Magnetic field dependence on the polarization of bis(O,O'-dialkyldithiophosphoryl)disulfide in the reaction of zinc(II) dithiophosphate with hydroperoxide in chlorobenzene at 343 K.

Our investigations have also shown that the polarization pattern depends on the kind of metal. The reaction of zinc dithiophosphate complexes with hydroperoxide leads to formation of bis(O,O'-dialkyldithiophosphoryl)disulfide with an emission signal (emm.), whereas in the reactions of nickel(II) and copper(II) complexes an absorption polarization (abs.) is created. This behaviour is explained by the loss of spin memory of the radical emerging from radical pair **I** caused by the shortening of the relaxation time in the presence of paramagnetic metal ion, and this and the radical pair can be considered as a diffusion radical pair (F*-pair). The change of the radical pair multiplicity results in a change in the polarization sign according to CIDNP theory.

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References

1 R. M. Gainullin, I. E. Ismaev and A. V. Il'yasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2215 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, 2212).
2 R. M. Gainullin, A. V. Il'yasov, V. M. Bashinova and F. N. Mazitova, *Khim. Fiz.*, 1991, **10**, 1109 (in Russian).
3 A. Vaisberg, *Organicheskie rastvoriteli (Organic solvents)*, Izd. Inostrannaya Literatura, Moscow, 1969, p. 378 (in Russian).
4 B. D. Krugalov and B. I. Golovenko, *Sovmestnoe poluchenie fenola i atsetona (Combined preparation of phenol and acetone)*, Goskhimizdat, Moscow, 1963, p. 38 (in Russian).
5 O. N. Grishina, V. M. Bashinova, N. P. Anoshina and F. Ja. Jusupova, *Neftekhimiya*, 1976, **16**, 609 (in Russian).
6 R. M. Gainullin, PhD Thesis, Kazan, 1992.
7 *EPR svobodnykh radikalov v radiatsionnoi khimii (EPR of free radicals in radiation chemistry)*, Khimiya, Moscow, 1972, p. 244 (in Russian).
8 J. A. Howard, Y. Ohkatsu, J. H. B. Chenier and K. U. Ingold, *Can. J. Chem.*, 1973, **51**, 1543.

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