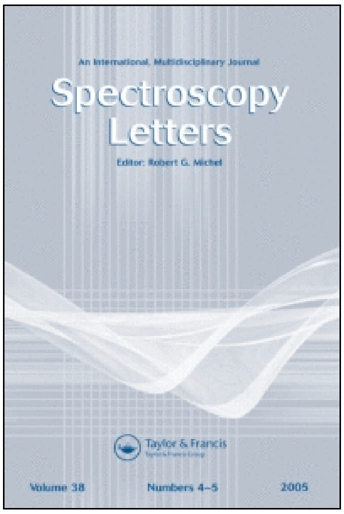

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Inducing Dynamic Nuclear Polarization in Chemical Reactions

S. V. Rykov[a]; A. L. Buchachenko[a]; A. V. Kessenich[a]
[a] Academy of Sciences Moscow, Institute of Chemical Physics, USSR

To cite this Article Rykov, S. V. , Buchachenko, A. L. and Kessenich, A. V.(1970) 'Inducing Dynamic Nuclear Polarization in Chemical Reactions', Spectroscopy Letters, 3: 2, 55 — 58

To link to this Article: DOI: 10.1080/00387017008075695

URL: http://dx.doi.org/10.1080/00387017008075695

SPECTROSCOPY LETTERS, 3(2), 55-58 (1970)

INDUCING DYNAMIC NUCLEAR POLARIZATION IN CHEMICAL REACTIONS

KEY WORDS: the decomposition of peroxides,CINDP.

S.V.Rykov,A.L.Buchachenko,A.V.Kessenich

Institute of Chemical Physics,Academy of Sciences
Moscow V-334,USSR

The experimental studies of the dynamic nuclear polarization in the chemical reactions(CINDP) [1-11] discover some characteristic peculiarities - the unusual behaviour of the spin multiplets, the appearance of nuclear polarization in the products of cage radical recombination, and finally, the dependence of the sign of polarization upon the type of reaction in which the radical participates. These pecularities are specific for CINDP and differentiate CINDP from the ordinary two-frequency dynamic nuclear polarization.

The last specific figure shows very clearly that the suggestion that the nuclear polarization arises in free radicals is insufficient for the explanation of CINDP. Indeed from this point of view it is not possible to explain why methyl radicals bring the negative polarization in the recombination products and the positive polarization in the products of abstraction reactions 12 . It is not excluded that the nuclear polarization arises in the elementary chemical reactions of birth and disappearing of the radicals. We have carried out some experiments in order to verify these ideas.

At the decomposition of benzoyl peroxide in C_2Cl_4 at 120°C in the presence of CH_3I(0,1M) the methyl containing products are formed (see Table 1).

Table 1. The methyl containing products.

Products	(ppm)	Polarization
CH_4	0,13	A
CH_3-CH_3	0,83	E
$C_6H_5CO_2-CH_3$	3,8(CH_3)	E
$C_6H_5-CH_3$	2,32(CH_3)	E

A: enhanced absorption; E: emission.

It is evident that in this case the methyl radicals are formed at the reaction of phenyl (or benzoyl) radicals with CH_3I. So in this case the methyl radicals are formed as an individual species but not from the radical pairs in cages, as it is at the decomposition of methyl containing peroxides. In spite of this the signs of nuclear polarization coincide with ones in the same products formed at the decomposition of peroxides.

These results show that the sign of the nuclear polarization does not depend on whether the radicals are formed as an individual species or escape from the radical pairs in cages.

We have studied also the decomposition of bicyclohexylpercarbonate,peracetylisopropilcarbonate and some azocompounds in CCL_4. In all of these reactions chloroform is formed. The scheme of $CHCl_3$ formation may be described in the following way:

peroxide (or azocompound) $\dot{R}$ (1)

$\dot{R} + CCl_4 \quad RCl + \dot{C}Cl_3$ (2)

$\dot{C}Cl_3 + HX \quad HCCl_3 + \dot{X}$ (3)

$\dot{C}Cl_3 + HX \quad HCCl_3 + \dot{X}$ (4)

In all cases the protons of chloroform have a strong negative nuclear polarization. As the proton in molecule $CHCl_3$ was not connected with a free radical it is possible to conclude whether the polarization of this proton arises in the reaction (3) or the polarization transfers to chloroform from other molecules as it follows from the reaction (4).

The second suggestion should be excluded because chloroform is the only product exhibiting the strong polarization at the decomposition of bicyclohexylpercarbonate in CCl_4. The polarization of protons of any other products is not discovered.

Moreover, the saturation of protons of all products with the exception of $CHCl_3$ at the time of reaction does not change the proton polarization of chloroform.

These results confirm the idea that nuclear polarization is induced in the elementary stages of chemical reactions, e.g. at the moments when strong electron-electron and electron-nuclear interactions exist, when the reconstruction of electronic clouds of interacting molecules occurs [12]. It opens new possibilities of studying the physics of the elementary chemical reactions.

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Received February 11, 1970