CIDNP of ^{13}C and ^{1}H Nuclei in the Reactions of Cyclohexadienone Carbenes*

G. A. Nikiforov, Sh. A. Markaryan, L. G. Plekhanova, B. D. Sviridov, S. V. Rykov, V. V. Ershov and A. L. Buchachenko
Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow B-334, *USSR*

T. Pehk, T. Saluvere and E. Lippmaa
Institute of Cybernetics of the Estonian Academy of Sciences, Tallinn 200001, *USSR*

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Abstract—Thermal decomposition of 4-diazo-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one in perhalogenated solvents has been investigated. The decomposition reaction proceeds via a carbene intermediate first to a singlet and then to an effectively triplet free encounter radical pair formed in a halogen abstraction reaction. The polarisation of the stable reaction product is determined by competing processes in the primary cage, intersystem crossing and escape from the cage.

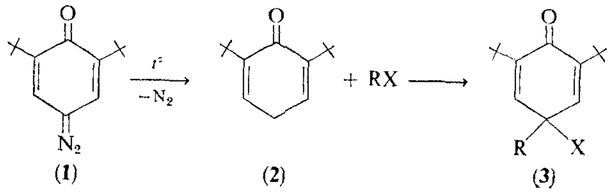
INTRODUCTION

THERMAL or photochemical decomposition of diazocyclohexadienones and some other types of related compounds leads to the formation of very reactive carbene intermediates that may add to unsaturated compounds, forming three-membered rings,[1] or become stabilised through hydrogen- or halogen-abstraction reactions as well as molecular rearrangement. In inert solvents the derivatives of diphenylquinone are formed as the main product.[2] The carbene intermediate gives a complicated electron resonance spectrum which is characteristic of its triplet ground state.[2] The state actually participating in some addition reactions ought, however, to be more of a singlet nature, or a biradical, because *cis*- and *trans*-alkenes give different reaction products in addition reactions. If the intermediate carbene reacted in its pure triplet ground state, a mixture of products would be expected.[1,2]

Spin multiplicity is one of the most important characteristics of the intermediate carbenes, determining the course of such free radical reactions. Since Closs and Trifunac[3] have suggested that the spin multiplicity of a carbene which is involved in an abstraction reaction determines the spin multiplicity of the resulting radical pair, chemically induced nuclear spin polarisation (CIDNP) can be used to assign the singlet or triplet multiplicity to the reacting carbene[4,5,6] applying the basic rules of the CKO theory.[7 to 10]

EXPERIMENTAL

In this paper we want to report the results of our study of thermal decomposition of 4-diazo-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one in a 14 kG magnetic field. Our work on the thermal decomposition of this compound in various solvents was begun several years ago and it was shown that the corresponding cyclohexadienone carbene was the intermediate in all cases,[11,12,13] but only application of the CIDNP technique allowed us to establish the detailed mechanism of the reactions involved.[14] 4-Diazo-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one was thermally decomposed in perhalogenated solvents (tetrachloromethane, hexachloroacetone and trichlorobromomethane), saturated hydrocarbons (cyclohexane, *n*-heptane), alkenes (cyclohexene, *n*-heptene-1) and dioxane. Chemical polarisation of the reaction products resulted only in the halogenated solvents, where halogen abstraction leads to formation of the corresponding cyclohexadienone derivative with nearly quantitative (>85%) yield.



(1) (2) (3)

+ = *t*-Bu.
R = CCl_3; CCl_2COCCl_3.
X = Cl, Br.

All carbon-13 atoms (even those of the *tert*-butyl groups) are polarised in the thermal reaction product with hexachloroacetone and the whole polarisation pattern is inverted upon addition of isopropyl iodide, thus pointing to a primary reaction of **1** in a singlet state.[14] In proton spectra, only the *meta*-protons of the cyclohexadienone ring are polarised, showing a single emission signal during thermal decomposition of **1** in carbon tetrachloride (see Fig. 1). This result means that the precursors of the stable cyclohexadienone compounds are triplet radical pairs or pairs formed by encounters of free radicals with uncorrelated spins. Indeed, it follows from the simple rules for the sign of the polarised line as given by Kaptein,[9] that in a high field an emission line results for the *meta*-protons of a recombination product (+*E*), with $A_{meta} > 0$ and $\Delta g = 2{\cdot}0040 - 2{\cdot}0091 < 0$ only in this case. The *g*-factor of the phenoxy radical is 2·0040[15] and that of the trichloromethyl radical 2·0091.[5]

RESULTS AND DISCUSSION

The ^{13}C CIDNP-spectrum is shown in Fig. 2. All lines are polarised in the decomposition reaction of **1** in hexachloroacetone (HCA) at 120°C (0.5 g of **1** in 4 g of HCA). The spectrum is much more informative than the corresponding ^{1}H spectrum, showing that the intermediate substituted chlorophenoxy radical is characterised by a strong delocalisation of the unpaired electron. All lines with $A_i > 0$ show emission and those with $A_i < 0$, enhanced absorption.

The observed polarisation signs left open the nature of the primary precursor pair and of the carbene itself. To establish the spin multiplicity of the carbene, experiments with the addition of alkyl iodides (methyl iodide, ethyl iodide and isopropyl iodide) were carried out. The emission signal of the *meta*-protons diminishes with increasing iodoalkane concentration, goes to zero at about 0·4 mol/l RI concentration and thereafter changes into enhanced absorption. The whole ^{13}C polarisation pattern

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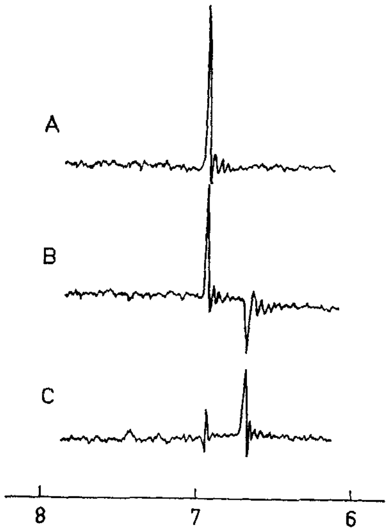


FIG. 1. Thermal decomposition of 4-diazo-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one in CCl_4. Proton spectra: (A) before the reaction; (B) during the reaction and (C) after the reaction.

changes in a similar manner and in addition to the polarised lines of the reaction product **3** the lines of the polarised alkyl iodide appear (see Fig. 3). The observed phenomena can easily be interpreted in terms of a competition between the S-precursor polarisation of spin-correlated pairs and the opposite T-precursor or F-type polarisation due to free-radical encounters of uncorrelated chloro phenoxy and the $\cdot CCl_2COCCl_3$ or $\cdot CCl_3$ radicals respectively.

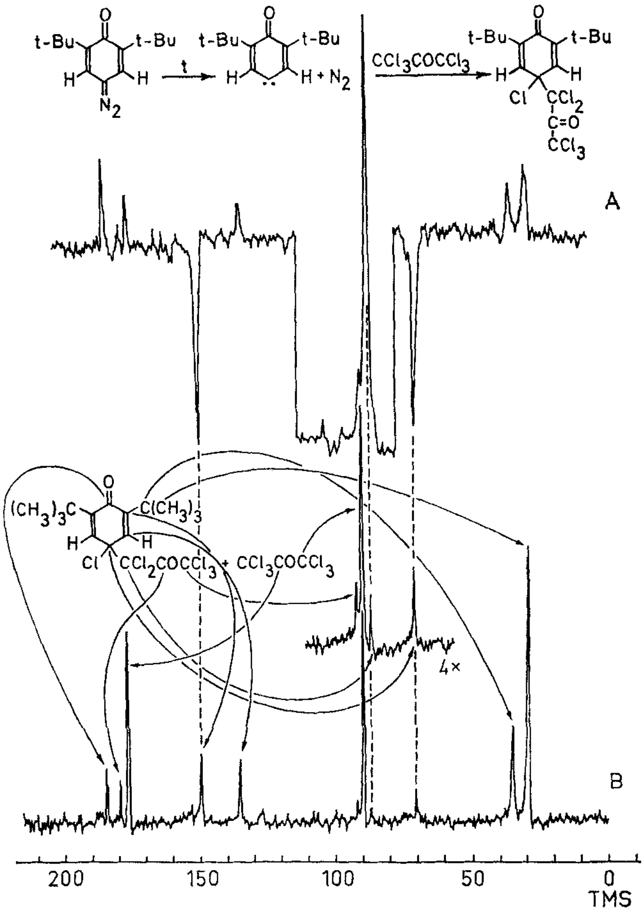


FIG. 2. Thermal decomposition of 4-diazo-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one in hexachloroacetone. Carbon-13 spectra: (A) during the reaction and (B) after the reaction. On the insert, ^{13}C spectrum of a fourfold concentrated solution of the same reaction product.

The reaction mechanism is given in Scheme 1. I follows from Scheme 1 that thermolysis of **1** leads a first to the formation of a singlet carbene **2** with an unusual electron structure (one unpaired electron on a σ-orbital and the other on a π-orbital), which reacts with the solvent, with halogen abstraction and formation of a singlet pair. Cage recombination in the pair leads to **3**, with positive or zero polarisation of the *meta*-hydrogens, depending on the cage lifetime and on the nuclear relaxation times. A fraction of the radicals undergoes intersystem crossing or escapes from the cage, leading to the formation of free encounter (F) pairs and to the same product **3**, but with an opposite polarisation of all nuclei, both ^{13}C and the *meta*-protons.

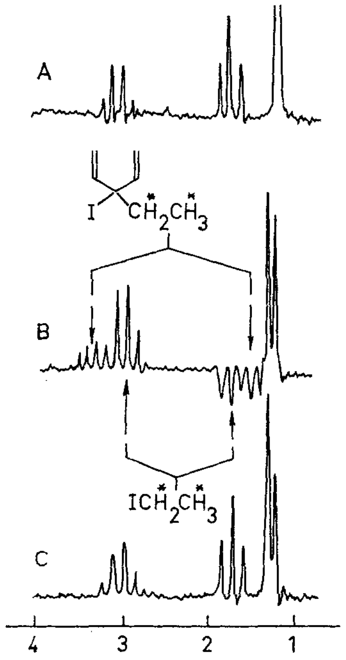
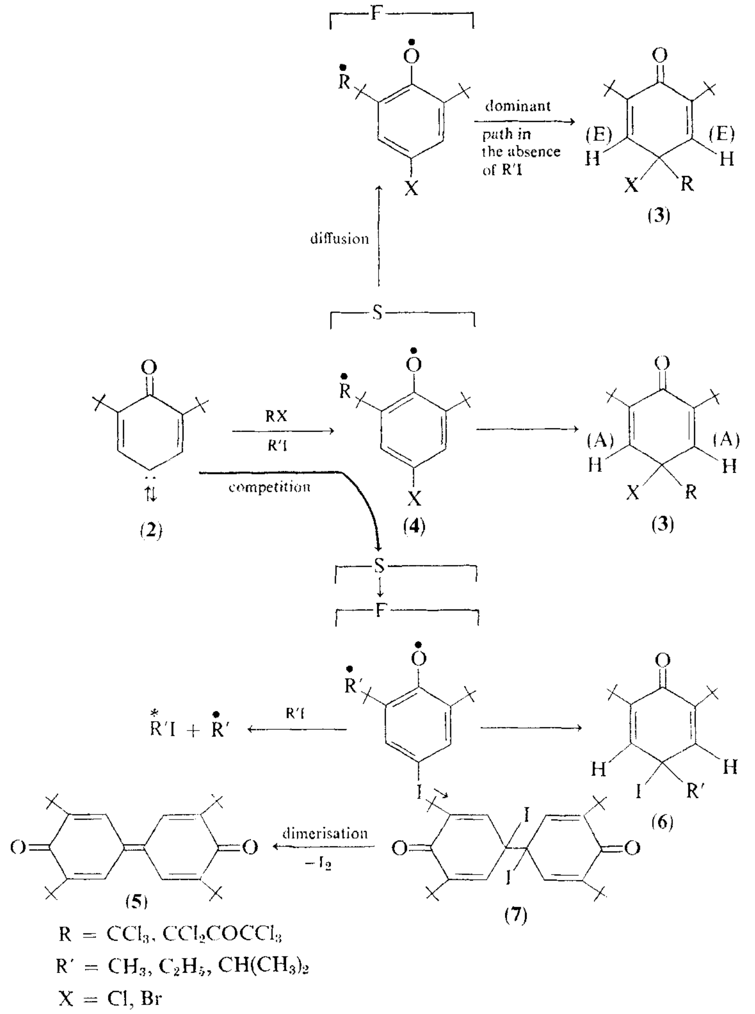


FIG. 3. Thermal decomposition of 4-diazo-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one in CCl_4 with the addition of ethyl iodide. Proton spectra: (A) before the reaction; (B) during the reaction and (C) after the reaction.

There are some changes in the chemistry of the thermal decomposition reaction upon the introduction of iodides. Increasing concentration of alkyl iodides in the perchlorinated solvent leads to an increased yield of the substituted diphenylquinones (**5**). Thermal decomposition of **1** in pure alkyl iodide leads to a nearly quantitative (92 to 95%) formation of the diphenylquinone. At the same time some products of iodoalkane addition to the carbene appear in the reaction mixture. The total content of these compounds (**6**) does not exceed 5 to 8 percent and does not increase upon any further increase in the iodoalkane concentration. In the proton resonance spectra some new enhanced absorption lines appear, corresponding to the *meta*-protons of the iodine derivative **6**, and in the region from 1·5 to 2 ppm the polarised lines of the geminal alkyl group (ethyl or isopropyl) in the same compound can be seen, where the methylene and methine protons with $A < 0$ show enhanced absorption and those of the methyl group with $A > 0$–emission (see Fig. 3). Carbon-13 spectra



SCHEME 1

of the reaction mixture (thermal decomposition of **1** in hexachloroacetone in the presence of isopropyl iodide) do not contain any observable lines of **6**, but show strong polarisation of the added iodoalkane along with that of **3**. In addition to this, the spectrum registered during decomposition in the presence of methyl iodide contains a singlet emission signal of the ethane protons. The presence of ethane in the reaction mixture was also proved by GLC.

In the presence of iodides the carbene **2** reacts predominantly with them, because of the lower energy of the C—I bond in comparison with that of C—Cl. Such competition leads to a less pronounced reaction with the perchlorinated solvent, and to a smaller yield of **3** from both the singlet pairs and especially the free encounter pairs. At high iodide concentrations after the polarisation sign reversal, all the polarised product **3** is formed from the original singlet pairs. In the singlet pairs formed in the reaction with the iodides no cage recombination occurs; the radicals escape and undergo secondary reactions, such as the free encounter formation of **6**, and dimerisation to **5** via the diiodo derivative. An increased iodide concentration understandably leads to enhanced formation of **7**. The primary alkyl radicals can react with alkyliodide molecules, leading to polarisation of this compound and recombine in free encounter pairs, with the formation of **6**. In accordance with this picture, the polarisation signs in the recombination product **6** and in the alkyl iodides must be the same. The experiment confirms this (see Fig. 3). Some alkyl radicals can, of course, also escape from the free encounter pairs, leading on recombination to ethane emission in experiments with the addition of methyl iodide. It must be concluded that both in thermal and photochemical[15] decomposition of **1** a singlet carbene is formed at first, and then various cage and escape reactions as well as intersystem crossing appear at comparable rates. In fact, even the main product of the reaction is polarised predominantly in secondary reactions during free encounters of the free radicals.

The true coefficient of nuclear polarisation E can be calculated from the kinetic equation for the apparent polarisation coefficient K.

$$K = \frac{I - I_0^{\infty}}{I_0^{\infty}} = \frac{Ek - T_{1n}^{-1}}{T_{1n}^{-1} - k}\,(e^{-kt} - e^{-T_{1n}t^{-1}}) - e^{-T_{1n}t^{-1}} \tag{1}$$

where k is the reaction rate constant and T_{1n} the nuclear spin-lattice relaxation time.

If $k \ll T_{1n}^{-1}$, as is usual for the diazocyclohexadienone (**1**) decomposition where at 95°C in carbon tetrachloride $k^{95} = 2 \times 10^{-4}\ s^{-1}$ (from UV-spectroscopic data $k^{95} = 2{\cdot}7 \times 10^{-4}\ s^{-1}$ at 95°C in carbon tetrachloride) and $T_{1n} \approx 5$ s, then at $t > t_{\max}$

$$K \simeq (EkT_{1n} - 1)e^{-kt} \tag{2}$$

This simple formula describes well the polarisation behaviour of the *meta*-protons during the thermal decomposition of **1** in CCl_4 and leads to $E = -(1000 \pm 300)$ for the true *meta*-^{1}H polarisation coefficient. The

^{13}C nuclear polarisation coefficients are smaller; $E = 620 \pm 200$ for the CCl_2 group in the pentachloroacetone group and $E = -210 \pm 60$ for the adjacent CCl group of the ring in the reaction product of **1** with hexachloroacetone.

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