CHEMICAL POLARIZATION OF NUCLEI IN REACTIONS OF CYCLOHEXADIENONE CARBENES WITH HALOGEN-CONTAINING ORGANIC COMPOUNDS

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One of the basic problems of carbene chemistry is the establishment of the electronic structure of the intermediate carbene responsible for the further course of the process. The experimental and theoretical development of the method of chemically induced polarization of nuclei CPN [1] opened up new possibilities for its solution.

Earlier we investigated the thermolysis of 2,6-di-tert-butyl-p-benzoquinone diazide (I) in various media [2-4]. It was shown that a common factor in all cases is the intermediate formation of a cyclohexadienone carbene (II), which, interacting with the medium, leads to the final reaction product. A definitive establishment of the mechanism of one reaction or another would be impossible without a knowledge of the multiplicity of the reacting carbene.

The purpose of this work was to investigate by the CPN method the electronic structure of cyclohexadienone carbenes at the moment of their interaction with halogen-containing organic compounds (HOC): CCl_4, CCl_3Br, CCl_3COCCl_3, CH_3I, CH_3CH_2I, and $(CH_3)_2CHI$.

In entirely halogenated hydrocarbons, the basic products of thermolysis of the quinone diazide (I) are cyclohexadienone derivatives (III) with a halogen atom as one of the geminal substituents (their yield is 85-90%) [4]. In an analysis of the PMR spectra of the reaction mixtures, negative polarization on the meta-proton of the ring of cyclohexadienone derivatives (III) was detected (Fig. 1). This indicates that the reaction of thermolysis of the quinone diazide (I) in HOC medium proceeds (at least partially) by a radical pathway according to a stripping–recombination mechanism. Evidently, the interaction of the carbene (II)

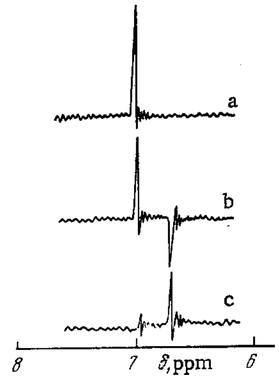

Fig. 1. PMR spectra of the reaction mixture in the thermolysis of 2,6-di-tert-butyl-p-benzoquinone diazide in CCl_4 medium at the beginning (a), during (b), and at the end of the reaction (c).

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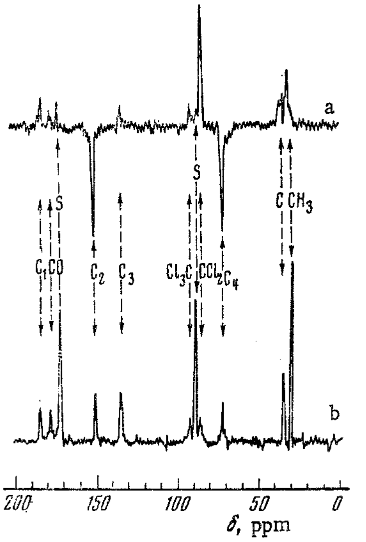


Fig. 2

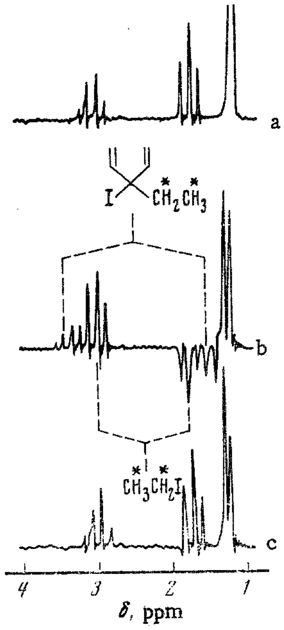
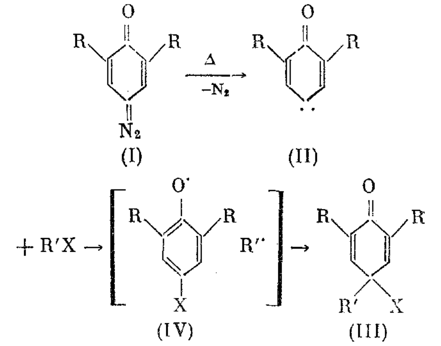


Fig. 3

Fig. 2. NMR-^{13}C spectra of reaction mixtures in the thermolysis of 2,6-di-tert-butyl-p-benzoquinone diazide in hexachloroacetone medium after 90 sec of heating (a) and at the end of the reaction (b). For (IV, X = Cl) : $\Delta g < 0$, $a_1 > 0$, $a_2 > 0$, $a_3 < 0$, $a_4 > 0$. For $CCl_3COC \cdot Cl_2$: $\Delta g > 0$, $a > 0$.

Fig. 3. PMR spectra of the reaction mixtures in the thermolysis of 2,6-di-tert-butyl-p-benzoquinone diazide in CCl_4 in the presence of ethyl iodide at the beginning (a), during (b), and at the end of the reaction (c).

formed with the substrate leads to the appearance of a radical pair, consisting of a 4-chloro-2,6-di-tert-butylphenoxyl radical (IV) and a radical of a halogenated solvent, the recombination of which gives the compound (III), carrying polarization on the meta-protons



$R = (CH_3)_3C$; $R' = CCl_3$, CCl_2COCCl_3; $X = Cl, Br$

According to the theory of CPN, the sign of the polarization is determined by the type of elementary chemical reaction of formation of the polarized product, by the value of the constants of hyperfine interaction (HFI) of the basic radical, and by the ratio of the g-factors of the components of the radical pair. For the phenoxyl radical (IV), the g-factor is equal to 2.004 [5], and the HFI constant $a > 0$. If we consider that the g-factor of the trichloromethyl radical (the case of thermolysis in CCl_4) is equal to 2.009 [6], i.e., $\Delta g < 0$, then in accord with the rules of selection according to nuclear spin in $S \rightarrow T_0$ transitions in radical pairs, the meta-protons of the cyclohexadienone ring will be negatively polarized in the recombination product (III), if its formation was preceded by radical pairs with uncorrelated spins or triplet radical pairs. The formation of one radical pair or another is determined by the multiplicity of the reacting carbene: a triplet pair arises with the participation of the triplet form of carbene, a singlet pair is generated by the singlet form of carbene. Finally, radical pairs with uncorrelated spins are formed in random encounters of radicals escaped from the primary radical pairs.

The data obtained on the CPN of protons are in good agreement with the results of an investigation of the CPN of ^{13}C in the thermolysis of the quinone diazide (I) in hexachloroacetone (Fig. 2). In agreement with the theory of CPN, emission is observed on nuclei of ^{13}C with $a > 0$, while an increase in the absorption is observed on nuclei with $a < 0$.

Since it is known [7] that the ground state of cyclohexadienone carbenes is a triplet state, it is not very probable that triplet—singlet inversion of the electronic structure of carbene would occur under the conditions of the reaction. Evidently, when nitrogen is eliminated from the quinone diazide (I), a cyclohexadiene carbene (II) arises, which reacts with the substrate in its singlet form, giving a primary singlet pair (RP_S). The radicals of this pair can recombine with the formation of the product (III), and can also escape into the volume and subsequently give pairs with uncorrelated spins (RP_U) in random encounters. In the first case, absorption should be observed on the meta-protons of the product (III), and in the second case emission [8]. Evidently the polarization observable experimentally on these protons is a summary effect, and the polarization created in pairs with uncorrelated spins (emission) predominates.

This hypothesis is confirmed by an experiment with the addition of alkyl iodide (CH_3I, C_2H_5I, and i-C_3H_7I) to the basic solvent. An analysis of the PMR spectra of the reaction mixtures obtained in the thermolysis of the quinone diazide (I) in a medium of entirely halogenated hydrocarbons in the presence of various amounts of alkyl iodide showed that as the concentration of the alkyl iodide increases in the initial mixture, the emission observed on the meta-protons of the cyclohexadienone compounds (III) decreases. At sufficiently high concentrations of the alkyl iodides ($[(I)] = 0.5$; $[R'I] = 0.4$ M), there is a reversal of the sign of polarization on the meta-protons of compounds (III). The same reversal was observed in an investigation of the CPN of ^{13}C in the reaction of thermolysis of the quinone diazide (I) in hexachloroacetone. Evidently, when alkyl iodides, which are radical acceptors, are added to the basic solvent, the concentration of radicals that have escaped into the volume (especially $^\bullet CCl_3$ or $^\bullet CCl_2COCCl_3$) decreases; the contribution to the polarization from the recombination of secondary pairs with uncorrelated spins (RP_U) correspondingly drops. At a sufficiently large content of alkyl iodides in the initial mixture, the observable absorption on the meta-protons is due to the fact that the dienone (III) is formed only from primary singlet radical pairs (RP_S).

With increasing concentration of alkyl iodides in the basic solvent, the yield of the diphenoquinone (V) increases, and in the thermolysis of the quinone diazide (I) in pure alkyl iodides it is 92-95%. At the same time, products of the interaction of the carbene with alkyl iodides (VI) appear in the reaction mixture. It is noteworthy that the content of compounds (VI) in the reaction mixture does not exceed 5-8% (according to the data of PMR spectroscopy) and does not increase with increasing concentration of alkyl iodides. In accord with this, in the PMR spectra, positively polarized signals from the meta-protons appear in the region of 6-7 ppm, and polarized signals from the protons of the geminal alkyl substituent of compounds (VI) appear in the region of 1.5-2 ppm; moreover, the CH_3 groups ($a > 0$) carry negative polarization, while the CH and CH_2 groups ($a > 0$) carry positive polarization (Fig. 3).

When ethyl or isopropyl iodide is used as an additive to the basic solvent, signals from polarized ethyl and isopropyl iodide are also detected in the PMR spectra of the reaction mixtures; moreover, the protons of the methyl groups ($a > 0$) proved to be negatively polarized, while the protons of the CH_2 and CH groups ($a < 0$) were positively polarized (see Fig. 3). The latter indicates that the polarization of the protons of alkyl iodides is created in the primary singlet radical pair (RP_S) on account of the escape of alkyl radical residues into the volume, followed by relay transfer of valence in the reaction of alkyl radicals with alkyl iodide molecules.

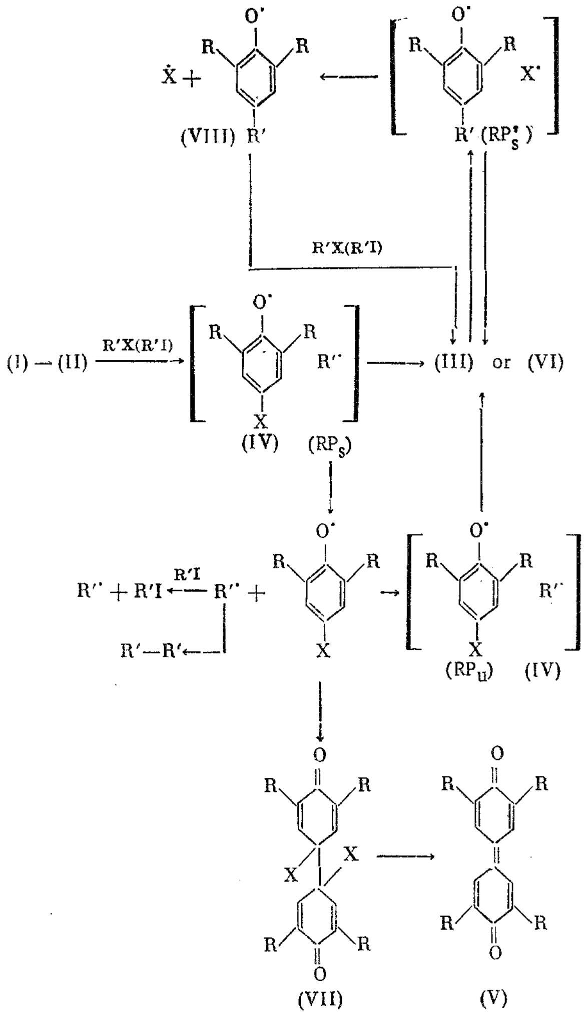
It should be noted that the protons of alkyl substituents of geminal compounds (VI) (products of recombination) and alkyl iodides (products of radicals that have escaped into the volume) possess polarization of the same sign. According to the CPN theory [1], the signs of polarization of the protons of the substances formed during recombination and on account of the escape of radicals from the same pair should be opposite. Since the polarization of alkyl iodides can be created only in primary singlet pairs (RP_S), it can be asserted that the observable polarization of the protons of the geminal products (VI) is the summary effect and is created both in the primary singlet pairs (RP_S) and on account of a different radical pathway of their formation.

Actually, the quinolide compounds (VI), containing an iodine atom in the gem-position, are extremely unstable, and eliminate it readily upon heating, with the appearance of phenoxyl radicals (VIII). The latter can interact with alkyl iodide molecules with the formation of the same geminal derivatives (VI). However, the polarization on their protons will be opposite to that which is created in the initial singlet pairs (RP_S).

Judging by the signs of the polarization, it makes a large contribution to the summary polarization of the compounds (VI).

Finally, the PMR spectrum of the reaction mixture, when CH_3I is added to the basic solvent, contains a weak singlet signal from the protons of ethane, the presence of which in the mixture is also confirmed by the method of gas chromatography. The formation of ethane is evidently the result of dimerization of the methyl radicals that escaped into the volume from the primary singlet pair (RP_S).

Thus, the general process of thermolysis of the quinone diazide (I) in halohydrocarbons can be represented by the scheme. In the thermolysis of the quinone dizide (I), a singlet carbene (II) is initially formed; as a result of the peculiarities of its electronic structure (localization of one of the nonbonding electrons on σ-orbitals, and the other on p-orbitals) it reacts with halogenated solvents with stripping of a halogen atom, followed by the appearance of singlet radical pairs (RP_S). The recombination of radicals in these pairs gives the product (III). A certain fraction of the radicals escape from the singlet pairs into the volume, which subsequently leads during their encounters to the appearance of pairs with uncorrelated spins (RP_U), in the recombination of radicals in which, the compound (III) is also formed.



$R = C(CH_3)_3$; $R' = CCl_3$ and CCl_2COCCl_3, X = Cl and Br (III);
$R' = CH_3$, C_2H_5 and $CH(CH_3)_2$, X = I (IV)

The interaction of the singlet carbene (II) with alkyl iodides initially also gives singlet pairs (RP_S), from which the compound (VI) can be formed during recombination. Moreover, the radicals from these pairs may partially diffuse into the volume. This leads to secondary reactions. Thus, 4-iodo-2,6-di-tert-butylphenoxyl radicals dimerize during collisions, with the formation of the geminal product (VII), which readily eliminates an iodine molecule, being converted to the diphenoquinone (V). On the basis of this, an increase in the concentration of alkyl iodides in the initial mixture should give an increase in the yield of the diphenoquinone (V), which was also noted above.

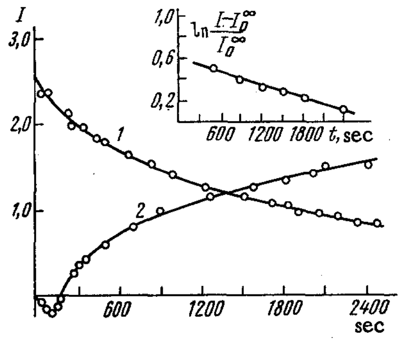


Fig. 4. Kinetics of CPN during the thermolysis of 2,6-di-tert-butyl-p-benzoquinone diazides in CCl_4: 1) (I); 2) (III).

Alkyl radicals (alkyl iodide residues) that have escaped into the volume participate in a relay exchange of an iodine atom with alkyl iodides, creating polarization of them. Moreover, in encounters with 4-iodo-2,6-di-tert-butylphenoxyl radicals, the alkyl radicals form pairs with uncorrelated spins (RP_u), recombination in which gives cyclohexadienone compounds (VI).

The latter in turn are capable of inducing 4-alkyl-2,6-di-tert-butylphenoxyl radicals (VIII) under the conditions of the reaction; they react with alkyl iodides, being converted again to the initial geminal derivatives (VI).

Thus, the data of CPN permit us to assert that in the thermolysis of quinone diazides, the reaction is carried only by the singlet form of the carbene, while the observed polarization in the basic product is the result of secondary processes, associated with the diffusion of radicals from the singlet radical pairs into the volume. This conclusion is in good agreement with the data on the investigation of the multiplicity of cyclohexadienone carbenes by the method of Skell and competing reactions [9].

Kinetic treatment of the CPN data for the thermolysis of the quinone diazide (I) in CCl_4 medium is cited in Fig. 4. The kinetic equation for the measurement of CPN in first-order reactions (or reducible to them) takes the form

$$K = \frac{I - I_0^\infty}{I_0^\infty} = \frac{Ek - T_{1p}^{-1}}{T_{1p}^{-1} - k}\,[\exp(-kt) - \exp(-T_{1p}^{-1}t)] - \exp(-T_{1p}^{-1}\cdot t),$$

where K is the coefficient of amplification; E is the true coefficient of amplification of CPN; k is the rate constant of decomposition of the quinone diazide (I); T_{1p}^{-1} is the relaxation time of polarized protons.

If $k \ll T_{1p}^{-1}$ (this case is realized in the decomposition of quinone diazide, $T_{1p}^{-1} \sim 5$ sec), then the shape of the PMR signal from the meta-protons of (III) at $t > t_{max}$ is described by the equation (see Fig. 4):

$$K = (EkT_{1p}^{-1} - 1)\exp(-kt). \tag{1}$$

An analysis of the kinetics of CPN according to Eq. (1) gives the coefficient of amplification of the polarization $E = -(1000 \pm 300)$ and rate constant of decomposition of the quinone diazide (I) $k\ 95° = 2 \cdot 10^{-3}$ sec^{-1}. The latter value is in good agreement with the rate constant of the decomposition of the quinone diazide (I) in CCl_4 obtained by the method of UV spectroscopy ($k\ 95° = 2.7 \cdot 10^{-3}$ sec^{-1}). The coefficient of polarization on the ^{13}C nuclei is lower, $E = 620 \pm 200$ for the CCl_2 group in the pentachloroacetone radical and $E = -210 \pm 60$ for the CCl group in the cyclohexadienone ring in the reaction of the quinone diazide (I) with hexachloroacetone.

EXPERIMENTAL METHOD

The CPN of the protons was investigated on a Varian DA-60-H high-resolution NMR spectrometer. The polarization on the ^{13}C nuclei was investigated on a YaR-1 spectrometer. The chemical shifts were counted relative to TMS.

The volume of the sample did not exceed 0.4-0.5 cm^3; automatic thermostatic control of the sample was accomplished with an accuracy of ±2° with respect to the volume of the sample. The temperature of the sample was established for 20-30 sec after placement of the sample in an air flow of set temperature. The temperature was varied in the interval 60-140°.

CONCLUSIONS

The thermolysis of 2,6-di-tert-butyl-p-benzoquinone diazide in a medium of halogenated hydrocarbons was investigated by the method of chemically induced polarization of nuclei. The cyclohexadienone carbene formed during thermolysis reacts with the medium in the singlet form, while the observed polarization is the result of secondary processes, associated with the diffusion of radicals from the primary singlet radical pairs into the volume.

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