potential of this radical was found to be 7.72 eV, and its IR spectrum in an argon matrix was recorded at 12 K.

2. Assignment of the IR bands of the radical to normal vibrations was proposed. The shifts in stretching vibration frequencies of the exocyclic C-C bond and in the benzene ring of the radical relative to perfluorotoluene was ascribed to delocalization of electron density in the benzyl system.

LITERATURE CITED

EPR STUDY OF PHOTOREDUCTION OF ADDUCTS OF 3,6-DI-TERT-BUTYL-O-BENZOQUINONE WITH DICHLOROCARBENE


The photoreduction of sterically hindered quinones and the properties of the thus-formed free radicals have been intensely studied lately. The interest in this field is illustrated by the efforts to clarify the degradative action of light on certain biological objects, and the role of quinones in the photosynthetic process. Moreover, the successful progress of research in the photochemistry of quinones led to the discovery of induced polarization of electrons in these systems [1]: the possibility of studying the free radicals thus formed was revealed, the properties of which are determined by the presence of certain donors. For example, the photoreduction of quinones in neutral media (hydrocarbons) leads to the formation of neutral semiquinone radicals (QH) as the result of splitting-off of a hydrogen atom from the solvent. In the presence of electron-donor molecules, anion-radicals (Q⁻) are formed by a one-electron transfer [2, 3]. The various organometallic derivatives of the semiquinone radicals are formed through photooxidation of metal complexes by quinones [4, 5]. These systems were found to be very suitable for studying solid-phase processes of hydrogen atom transfer in organic single crystals and in frozen solutions [6, 7].

The present work deals with the EPR study of radicals formed during the photoreduction of adducts of dichlorocarbene with 3,6-di-tert-butyl-o-benzoquinone. These adducts are obtained by the reaction of 3,6-di-tert-butyl-o-benzoquinone with chloroform in an alkaline medium [8].

Table 1 shows the hyperfine interaction (HFI) constants of an unpaired electron with magnetic nuclei in radical (I). The form of the spectrum does not change when the temperature is varied in the -120 to -20°C range (at higher temperatures, the EPR signal of (I) is not observed), which indicates the absence of dynamic effects due to intramolecular rearrangements of the (I) skeleton. Attention should be paid to the high value of HFI with a geminal hydrogen atom, and HFI with only one chlorine atom occurring by a hyperconjugation mechanism. Since the four ring carbon atoms of (I) have an sp² hybridization, it can be assumed that they are practically in the same plane. In this approximation, the structure of (I) can be represented in the form of an almost planar ring with inappreciable deviation of two sp³-hybridized carbon atoms from this plane.

In this situation, the cyclopropane ring deviates from the plane of the six-membered ring, being in a pseudoequatorial position, while the geminal hydrogen atom and the tert-butyl group occupy pseudoaxial positions. Thus, the overlap of the p-orbital carrying an unpaired