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Direct Characterization of Hexamethyl(Dewar Benzene) Radical Cation by Electronic Absorption Spectroscopy

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The electronic absorption spectrum of the hexamethyl(Dewar benzene) radical cation (**1**$^{•+}$) is presented for the first time. Partial stabilization of **1**$^{•+}$ in organic glasses at cryogenic temperatures is explained in terms of matrix rigidity, which can inhibit the isomerization process. Annealing of the matrix leads to fast isomerization of **1**$^{•+}$ to hexamethylbenzene radical cation (**2**$^{•+}$) and, at high concentrations of **1**, formation of the hexamethylbenzene dimer radical cation can be observed.

Introduction

The radical cations of the valence isomers, hexamethyl(Dewar benzene) **1** and hexamethylbenzene **2**, have long been the target of interest.[1−4] Particular efforts were undertaken to provide evidence for the existence of the primary radical cation of **1**. A first unambiguous though indirect proof was delivered by Roth et al.[4] by means of the chemically induced dynamic nuclear polarization (CIDNP) technique. Direct spectroscopic characterization of **1**$^{•+}$ was finally achieved by electron spin resonance (ESR) spectroscopy, indicating the $^2B_2$ state as its ground state.[5−8] However, the electronic absorption spectrum has never been measured for hexamethyl(Dewar benzene) radical cation.

Evidence of the stabilization of **1**$^{•+}$ in matrixes[5,7−9] or at room temperature on the surface of strong oxidants such as dioxygenyl hexafluoroantimonate[10] seems to be at odds with the results indicating its rapid spontaneous isomerization to **2**$^{•+}$.[1,3,4,11]

We have reported previously the results of pulse radiolytic studies on the **1**$^{•+}$ → **2**$^{•+}$ isomerization.[11] Delayed formation of the absorption of **2**$^{•+}$ ($\lambda_{max} = 508$ nm) observed after pulse radiolytic ionization of **1** embedded in a low-temperature (77−96 K) 3-methylpentane glass was attributed to the isomerization process. In contrast, ionization of **2** under similar experimental conditions led to the appearance of the absorption of **2**$^{•+}$ immediately after the electron pulse (Scheme 1). The kinetics of the isomerization process was monitored and it was possible to estimate the activation parameters associated with this process: $E_A = 4.2$ kcal/mol and $A = 1.3 \times 10^{10}$ s^{-1}.

However, it was noticed that yield of the formation of **2**$^{•+}$ was higher for a sample of irradiated **2** compared to **1** when both samples received the same radiation dose. This may indicate that under these experimental conditions only some of the primary formed **1**$^{•+}$ isomerized to **2**$^{•+}$. Therefore, an effort has been undertaken to characterize directly that part of the primary radical cation (**1**$^{•+}$) which seemed to be stabilized under these conditions.

Experimental Section

All chemicals were purchased from Aldrich and were purified by standard laboratory procedures as necessary.

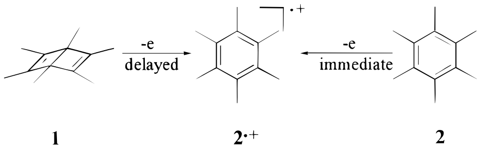
2-Chlorobutane or methylcyclohexane with 1-chlorobutane (1 M) acting as an electron scavenger were used as organic matrixes, which on freezing form transparent glasses suitable for optical measurements. These samples were prepared by immersing room-temperature solutions in liquid nitrogen. Neither methylcyclohexane nor 2-chlorobutane glasses were severely cracked. The samples were 2 mm thick and were placed in a temperature-controlled, liquid helium-cooled cryostat (Oxford Instruments). The desired temperature (10−100 K) of the matrix was accomplished by helium flow and automatically controlled heating. To achieve fast equilibration of the sample temperature the matrixes were directly exposed to the helium flow by removing the side walls of the sample cell.

The optical absorption spectra were measured on a Cary 5 spectrophotometer (Varian).

The samples mounted in a cryostat were irradiated with 4 μs electron pulses from an ELU-6 linear accelerator. Details of the pulse radiolysis system are given elsewhere.[12] Although precise dosimetry was not explicitly needed for the interpretation of the present work, it was known from the earlier investigations that the 4 μs electron pulse delivers a dose of 1 kGy. Strong absorption bands (as presented in Figures 1−4) were observed for samples that had received around 30 electron pulses, although no difference was distinguishable between results obtained for different irradiation doses, except for yield of products.

Photochemical reactions were carried out with a 450 W xenon arc lamp as a light source. Interference filters (Oriel) were used as indicated.

SCHEME 1



Results and Discussion

Radiolysis of **1** embedded in matrixes at different cryogenic temperatures allows observation of the product of isomerization, i.e., **2**$^{•+}$ (even at 10 K), although with different yield. However, what is even more important, the presence of a broad structureless absorption band with maximum around 930 nm can be noticed in these spectra. Its contribution to the spectrum

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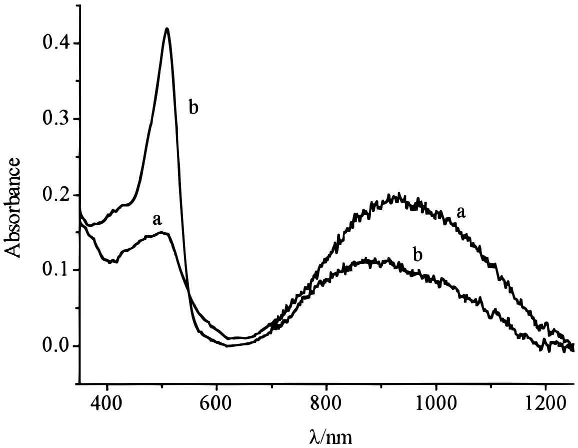
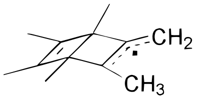


Figure 1. Absorption spectra of irradiated **1** (0.02 M) in a glassy matrix of 2-chlorobutane at (a) 10 K and (b) at 77 K (annealed sample irradiated previously at 10 K or directly irradiated at 77 K with the same radiation dose).

increases at lower temperatures at the expense of the absorption band of **2**$^{\bullet +}$ (see Figure 1). Below 50 K the ratio of both absorption bands does not undergo further changes, indicating that the process connecting both products of radiolysis is effectively inhibited. It has to be pointed out that there is almost no temperature dependence of the yield of **2**$^{\bullet +}$ upon radiolysis of hexamethylbenzene solution at different temperatures.

In light of ESR results that unambiguously characterize the presence of **1**$^{\bullet +}$ in rigid media, the absorption band at 930 nm can be assigned to the radical cation of hexamethyl(Dewar benzene). ESR spectroscopy indicated also that loss of a proton from **1**$^{\bullet +}$ in a bimolecular reaction with neutral **1** resulted in the formation of the allyl radical **3**$^{\bullet}$ in some matrixes.[7,8]



3$^{\bullet}$

However, the species observed at 930 nm cannot be due to the product of an intermolecular reaction since its yield decreases with annealing and softening of the matrix. Moreover, increasing the concentration of **1** in the irradiated sample by a factor of 10 resulted in identical proportions of both bands observed in the spectrum.

An assignment of the 930 nm band as due to matrix radical cations formed in the primary process of radiolysis can be ruled out since this band is observed in two different matrices whose radical cations show very different spectra (radical cations generated from 2-chlorobutane are very well characterized and absorb at ≈540 nm).[13,14] Also, ionization of **2** under the same experimental conditions indicated complete hole transfer from the matrix to the solute. For the same concentration of **1**, and taking into consideration that the ionization potential of **1** is lower than that of **2**,[2,15] the processes of charge transfer should be completed with similar efficiency.

On the other hand, an assignment of the observed absorption band to **1**$^{\bullet +}$ seems to be inconsistent with the photoelectron spectrum of **1** (the vertical energy difference of about 0.5 eV between the first two peaks in the PE spectrum[2] is much smaller that the energy of the presently observed optical transition of 1.35 eV in the radical cation). By analogy to the closely related case of the radical cation of norbornadiene, some changes in orbital energies introduced by distortions of the molecular geometry on ionization and electronic excitation, respectively, can readily explain this discrepancy.[16] The ground state of the radical cation of **1** was identified by means of ESR spectroscopy as a $^2B_2$ state and is characterized by a deficit of an electron in the antibonding combination of the two π orbitals [b_2, highest occupied molecular orbital (HOMO)]. This should express itself in a decrease of the repulsive interactions of two olefinic bonds in **1**$^{\bullet +}$ and therefore in a more bent structure compared to **1**. In contrast, absorption of light will promote an electron from the bonding (a_1, HOMO-1) to the antibonding combination of π-bond orbitals (b_2, HOMO), which results in a weakening of the attractive interactions and hence to a flattening of the structure. Additionally, the radical cation that results from removal of an electron from this orbital (a_1) possesses considerably weakened transannular bond.[2,4] As a result the energy gap between these orbitals should widen on going to the radical cation.

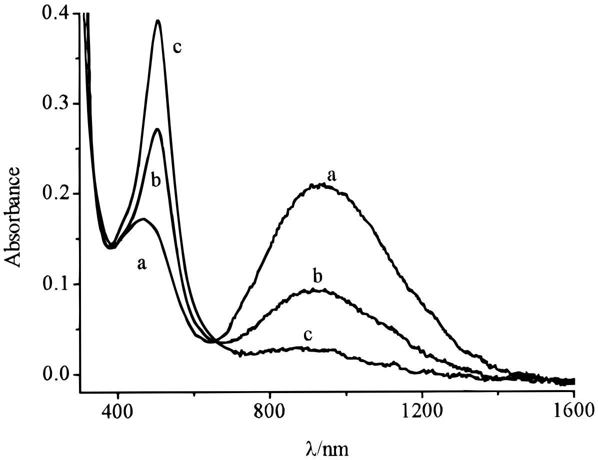


Figure 2. Absorption spectra of irradiated **1** (0.02 M) in a glassy matrix of methylcyclohexane [+1-chlorobutane (1 M)] measured (a) after irradiation and after subsequent illumination of the sample (950 nm interference filter) for (b) 2 min or (c) 5 min.

The assignment of the 930 nm absorption band to **1**$^{\bullet +}$ can be further supported on the basis of photochemical experiments. Bleaching of the irradiated sample of **1** at 10 K through 950 or 1000 nm interference filters is very effective and the disappearance of the 930 nm absorption band can be related to the simultaneous growth of the 508 nm band, which is assigned to the isomerization product, i.e., **2**$^{\bullet +}$ (see Figure 2).

The isomerization process triggered by light can also be observed upon annealing of the matrix. Increase of the matrix temperature above 50 K leads to the decay of the absorption of **1**$^{\bullet +}$ and a parallel growth of the absorption band of **2**$^{\bullet +}$. This experiment reveals additional interesting aspects of the kinetics of isomerization process in rigid media. As the temperature is raised to the successively higher levels, the decay of the 930 nm absorption band assigned to **1**$^{\bullet +}$ and the growth of the 508 nm absorption band of **2**$^{\bullet +}$ can be monitored during the first several minutes until the process reaches saturation, even though the isomerization process is not fully completed. Storage of the sample for several additional hours does not significantly change the ratio of both absorption bands attained at saturation. A similar reaction progress is observed in experiments where the radiolytic irradiation was conducted directly at a particular temperature (see Figure 1). Further reaction can be initiated only by further increase of matrix temperature i.e., the process is stepwise (see Figure 3). Of course the isomerization process can be frozen out at any moment by lowering the temperature.

The results presented in Figure 3 clearly demonstrate a matrix-site effect and reveal information on the influence of environ-

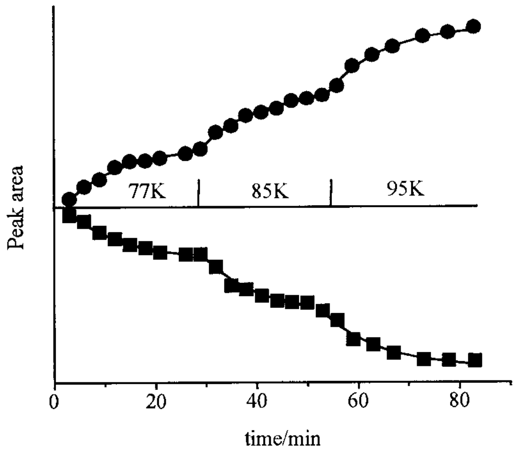


Figure 3. Changes in the intensities of the 508 nm (●) and 930 nm (■) absorption bands of an irradiated glassy matrix of 2-chlorobutane containing **1** (0.02 M) observed in time and upon subsequent changes of the matrix temperature above 77 K.

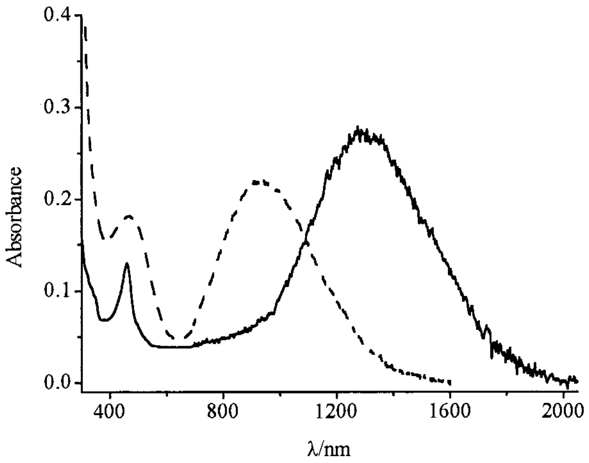


Figure 4. Absorption spectrum of the radical cation of hexamethylbenzene dimer observed after annealing (to 100 K) of irradiated matrix of methylcyclohexane [+1-chlorobutane (1 M)] containing **1** (0.1 M). Dashed line: spectrum a from Figure 2 presented for comparison.

mental factors on the unimolecular reaction. In rigid media, different molecules in a sample experience different microenvironments and as a result each site possesses a characteristic activation barrier for the reaction. This distribution of activation barriers among the matrix sites leads to dispersive kinetics of processes.[17,18] At different temperatures the reaction in different matrix sites can become observable on the time scale of the experiment. A striking feature illustrated by Figure 3, i.e., the fact that the decay and growth observed at consecutive temperatures have the same range of rate constants (they are similar in shape for all temperatures), is a simple consequence of this fact. By stepwise warming of the matrix to successively higher temperatures, subsequent layers are sliced off the distribution of activation energies and/or rates of reaction.

The distribution slicing methodology of Sponsler et al.[18] has been adopted to the analysis of activation energy distributions. Assuming a preexponential term of 1.3×10^{10} s^{-1} from our previous paper,[11] a Gaussian distribution of activation energies with a standard deviation of 0.6−0.9 kcal/mol and the most probable value for activation energy of 4.5−5 kcal/mol have been determined.

On the other hand, an analysis of the kinetics of the process in terms of dispersive kinetics with a time-dependent rate coefficient in the form $k(t) = Bt^{\alpha-1}$ [17] also indicates a quite broad distribution (0.8 kcal/mol) of activation energies estimated to be centered at 4.5 kcal/mol.

The results presented above can be considered only as estimates since both methods strongly depend on the temperature of the experiment and the definition of the starting time $t = 0$ of subsequent steps of the process. An uniform temperature of the matrix is reached by warming in a rather complex way and during a finite time, which makes a precise definition of the starting time impossible.

On the other hand, as the temperature is raised to successively higher levels, a selective softening of matrix cages of different sizes can take place. This suggests that the distribution of the matrix cages of different sizes could be directly related to temperature of the matrix, especially in the region close to its glassy transition. The isomerization process can be observed only in matrix cages of appropriate size or geometry while others stabilize the primary radical cation. Either matrix relaxation or an intrinsic activation barrier can be responsible for the observed kinetics of the isomerization.

In any event, the distribution of reaction rates clearly demonstrates that the activation barrier for the process is strongly affected by environmental factors. Although the matrix effects cannot be dissected from the reactivity of $\mathbf{1}^{\bullet+}$, the results mentioned above put some upper limits for an intrinsic activation barrier for isomerization of hexamethyl(Dewar benzene) radical cation and clearly indicate that matrix cages can inhibit the process to some extent.

Observation of a small amount of the product $\mathbf{2}^{\bullet+}$ even at 10 K does not necessary indicate that the intrinsic barrier of isomerization is very low. It is conceivable that $\mathbf{2}^{\bullet+}$ is formed due to excess energy liberated in the ionization process.[19] Despite the fact that dissipation of the excess energy in polyatomic rigid matrices is very fast, it is possible that some local annealing of the sample can also take place.[20]

The stabilizing effect of the matrix can be observed up to a temperature where softening of the matrix allows diffusion and, hence, intermolecular processes. Beyond this point the dimerization process can take place, and in both cases of ionized **1** or **2** the dimer radical cation of hexamethylbenzene ($\mathbf{4}^{\bullet+}$) is formed. As can be seen in Figure 4, besides the charge resonance band at 1300 nm previously assigned to this dimer,[21] an absorption band at 460 nm can be also ascribed to $\mathbf{4}^{\bullet+}$ on the grounds of its parallel behavior to the near-infrared (NIR) band. This combination of a strong NIR band accompanied by a band of smaller intensity in the visible region is very characteristic for dimer radical cations of benzene derivatives.[21]

In the case of irradiated frozen solutions of **2**, softening of the matrix allows diffusion and interaction of $\mathbf{2}^{\bullet+}$ with the neighboring parent molecule, which results in the formation of $\mathbf{4}^{\bullet+}$. In the case of **1**, dimerization is preceded by an isomerization process (reaction 1). The resulting $\mathbf{2}^{\bullet+}$ can

$$\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+} \tag{1}$$

$$\mathbf{2}^{\bullet+} + \mathbf{1} \rightarrow \mathbf{2} + \mathbf{1}^{\bullet+} \rightarrow \mathbf{2} + \mathbf{2}^{\bullet+} \tag{2}$$

$$\mathbf{2} + \mathbf{2}^{\bullet+} \rightarrow \mathbf{4}^{\bullet+} \tag{3}$$

interact with adjacent neutral molecules of **1**. Since the more strained benzene isomer possesses a lower ionization potential, it is possible that charge transfer takes place. It is followed by a very fast isomerization of $\mathbf{1}^{\bullet+}$ (reaction 2). Reaction 2 is postulated to explain the chain decomposition of hexamethyl(Dewar benzene) in photosensitized reactions in polar solvents,[22,23] in electrochemical oxidation,[22] or on the surfaces of some semiconductors.[24] In the still quite viscous medium of the annealed matrix, the dimerization can terminate a propagation of this chain reaction since it leads to the formation of $\mathbf{2}^{\bullet +}$ in close proximity to neutral **2**. Dimer radical cations $\mathbf{4}^{\bullet +}$ are formed in reaction 3.

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