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Structure and photochemical rearrangement of the 3,3-dimethylbut-1-yne radical cation

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The structure of the 3,3-dimethylbut-1-yne radical cation and its unusual photochemical rearrangement to the trimethylallene radical cation have been characterized by low-temperature matrix EPR spectroscopy and DFT calculations.

Organic radical cations are very important intermediates in oxidative chemical transformations. The structure and reactivity of hydrocarbon and functional radical cations were studied extensively by EPR spectroscopy using a Freon (halocarbon) matrix technique.[1–4] The radical cations of unsaturated hydrocarbons (olefins and dienes) were among the first species characterized by this technique.[5] The dimethylacetylene radical cation and its thermal transformations were studied in halocarbon matrices[6] and zeolites.[7] The propyne radical cation was shown to give strong complexes with chlorine atoms of Freon molecules.[8] Meanwhile, to the best of our knowledge, the EPR spectra of isolated radical cations of acetylene and its monosubstituted derivatives (terminal alkynes) are still unavailable, although these species are of considerable theoretical interest and practical significance. In the case of acetylene, the complications may result from its high ionization potential (IP = 11.4 eV, *i.e.*, very close to those of Freons[9]) and a tendency to formation of dimers and multimers. An attempt to obtain the acetylene radical cation in a zeolite matrix yielded only a trimer (benzene radical cation).[10] The relatively high IP of propyne (10.4 eV) is probably responsible for the formation of a complex rather than an isolated radical cation in Freon matrices.[8] Here, we report the first observation of a radical cation produced from 3,3-dimethylbut-1-yne (*tert*-butylacetylene, TBAC) and discuss the photochemical behavior of this species. Note that TBAC has a lower IP (~9.9 eV[9]) and can be easily obtained in a monomeric form.

The experimental and computational methods were described in detail elsewhere.[11,12] The DFT calculations using PBE0 functional[13] were performed with a L22 basis set as implemented in the PRIRODA computational code.[14,15]

The TBAC radical cations were generated by X-ray irradiation of the frozen solutions of TBAC (0.1 to 2 mol%) in Freon 11 ($CFCl_3$), Freon 113 ($CF_2ClCFCl_2$) or Freon 113a (CF_3CCl_3). Irradiation, EPR measurements and photolysis were performed at 77 K. In all the cases, the EPR spectra were qualitatively similar. However, the best resolved spectra were obtained for dilute TBAC solutions in Freon 11, so we will restrict further consideration mostly to this case. The anisotropic multiplet spectrum (Figure 1) clearly indicates that *tert*-butyl group protons strongly contribute to the observed hyperfine structure. Quantum-chemical calculations for the primary TBAC radical cation $Me_3CC{\equiv}CH^{+\cdot}$ **1** at the DFT-PBE0/L22 level confirm this suggestion. An optimized structure (Figure 1) reveals a substantial delocalization of spin density between ethynyl and *tert*-butyl fragments with a marked elongation of a C–Me bond in the *tert*-butyl group (from 1.532 to 1.665 Å). The calculations predict major hyperfine coupling with ethynyl proton (strongly anisotropic with the principal HFC tensor components a_{xx} = = 2.68 mT, a_{yy} = 1.98 mT, a_{zz} = 0.86 mT) and one on the methyl protons of the *tert*-butyl fragment (roughly isotropic, a_{iso} = = 3.22 mT). In addition, two other pairs of methyl protons from the *tert*-butyl group should also exhibit measurable, nearly isotropic hyperfine coupling: $a_1(2H)_{iso}$ = 0.97 mT and $a_2(2H)$ = = 0.45 mT. Using these values as starting points, we have performed a series of simulations. The experimental spectrum could be reproduced reasonably well with the following set of parameters: a_{xx} = 2.5 mT, a_{yy} = 1.9 mT, a_{zz} = 1.0 mT (for ethynyl proton), $a(1H)_{iso}$ = 3.0 mT (for a strongly coupling 'selected' methyl proton), $a_1(2H)_{iso}$ = 0.8 mT and $a_2(2H)_{iso}$ = 0.75 mT

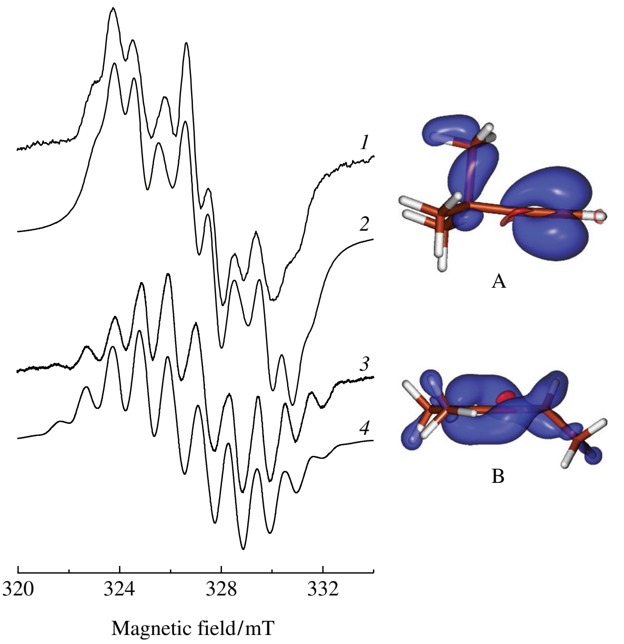

Figure 1 (*1*) EPR spectrum obtained by X-ray irradiation of TBAC frozen solution in Freon 11 at 77 K; (*2*) anisotropic simulation of the spectrum of TBAC radical cation (see text for parameters); (*3*) EPR spectrum obtained after photolysis of the TBAC radical cation at $\lambda > 500$ nm for 20 min; (*4*) the best-fit isotropic simulation of the trimethylallene radical cation (see text for parameters). Images A and B show the calculated spin density distribution in the TBAC and trimethylallene radical cations, respectively.

(for two pairs of other methyl protons). Actually, these parameters may be not very accurate because of a large number of variable parameters and certain oversimplifications in simulation (the neglect of small *g* anisotropy and HFC anisotropy for methyl protons, possible involvement of dynamic effects, *etc*.). Nevertheless, the overall spectral pattern is described adequately, which definitely supports its assignment to the primary TBAC radical cation characterized by the major hyperfine interaction of an unpaired electron with an ethynyl proton and a single proton of a non-rotating methyl group from the *tert*-butyl fragment. The hindered rotation of the methyl group in the EPR timescale in halocarbon matrices at 77 K was found previously for a number of hydrocarbon radical cations (*e.g.*, those of linear alkanes and isobutane[16]). Note that any possible product of a chemical transformation of the TBAC radical cation (rearrangement, fragmentation or dimerization) cannot account for the observed EPR spectrum.

The irradiated samples reveal an extensive violet coloration and remarkable photosensitivity. The transformation of the EPR spectrum occurs markedly under illumination at $\lambda > 600$ nm. Using light of $\lambda > 500$ nm leads to complete transformation after 20 min of photolysis under our experimental conditions. The resulting spectrum represents a well-resolved, nearly isotropic multiplet (at least, 11 lines) with an average splitting of ~1.1 mT (Figure 1). Note that the multiplet lines are actually not equidistant, which implies that the protons are magnetically nonequivalent. The observed signal should be ascribed to a product of rearrangement involving methyl group migration, in accordance with remarkable weakening of a specific C–Me bond in the primary TBAC radial cation. The theoretical analysis of possible products of such transformations reveals two principal possibilities (both thermodynamically favorable): migration of the Me group to the 2-position yielding the distonic type structure $Me_2C^+C(Me)CH^{\cdot}$ **2** and migration to the 3-position resulting in the trimethylallene radical cation $Me_2C{=}C{=}CH(Me)^{+\cdot}$ **3**. The quantum-chemical calculations for **2** yield the following set of isotropic HFC constants: $a(1H) = 0.78$ mT, $a_1(3H) = 0.26$ mT, $a_2(3H) = 0.23$ mT and $a_2(3H) = 0.06$ mT. This is completely inconsistent with the experimental spectrum, which exhibits much larger total spread and suggests significant HFC constants with all protons. On the other hand, in the case of **3**, the calculations demonstrate the extensive delocalization of spin density and relatively large HFC constants for all ten protons: $a(1H) = 2.33$ mT, $a_1(3H) = 1.08$ mT, $a_2(3H) = 1.07$ mT and $a_3(3H) = 0.87$ mT (assuming free rotation or pseudo-rotation of all methyl groups in the EPR timescale). It is clearly seen that the protons of two methyl groups exhibit virtually the same HFC constant, while for the third methyl group, it is about 20% smaller, which is in accordance with the spectral pattern. Using these values as initial parameters, we have performed an optimization of the isotropic simulation to fit the experimental spectrum using the WinSim software. The best-fit values are very close to the calculated constants (within 7%): $a(1H) = 2.5$ mT, $a(6H) = 1.14$ mT and $a(3H) = 0.84$ mT (the corresponding simulated spectrum is shown in Figure 1). Furthermore, the HFC values for methyl protons agree well with those reported for the tetramethylallene radical cation in various matrices[17] (this radical cation is also characterized by free rotation of methyl groups). Thus, the photoinduced transformation of the TBAC radical cation can be described by the following reaction:

$$\underset{\mathbf{1}}{Me_3CC{\equiv}CH^{+\cdot}} + h\nu \rightarrow \underset{\mathbf{3}}{Me_2C{=}C{=}CH(Me)^{+\cdot}}$$

Similar transformation also occurs in a CF_3CCl_3 matrix. The intramolecular migration of the methyl group is uncommon for the photochemistry of radical cations in halocarbon matrices.[18] Nevertheless, there is at least one more example of photoinduced methyl group migration in the case of the methyl *tert*-butyl ether radical cation.[19] Regarding the efficiency of the observed phototransformation, we did not make any quantitative estimates at this stage. However, it should be noted that the reaction is not accompanied by any substantial loss in the total number of paramagnetic species, which implies that the rearrangement is fast enough to compete favorably with photostimulated charge neutralization. The latter process typically dominates in Freon 11 (the characteristic quantum yields are of the order of 0.1[18]).

In summary, we have characterized the primary TBAC radical cation, which exhibits selective weakening of a specific C–Me bond and rather unusual photochemical rearrangement occurring *via* a low-lying excited state. These properties are very different from those characteristic of most known unsaturated radical cations (alkenes, dienes, *etc*.).

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