Diketone Radical Cations: Ketonic and Enolic Forms As Revealed by Matrix EPR Studies and DFT Calculations

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Received: December 12, 2006; In Final Form: February 10, 2007

Radical cations of 2,3-butanedione, 2,4-pentanedione, 3-methylpentane-2,4-dione, 2,5-hexanedione, and 2,3-pentanedione were investigated by electron paramagnetic resonance (EPR) spectroscopy in a solid Freon matrix and density functional theory (DFT) quantum chemical calculations. All the diketone radical cations in ketonic form show small proton hyperfine couplings (typically unresolved in the EPR spectra). In the cases of 2,4-pentanedione and 3-methylpentane-2,4-dione, enolic forms of the radical cations (π-type species with main spin population at carbon atom) were characterized. Preferential stabilization of the enolic form of 3-methylpentane-2,4-dione radical cation was explained by trap-to-trap positive hole migration rather than monomolecular relaxation of the ionized ketonic form through H atom transfer.

Introduction

Organic radical cations play a very important role in various chemical reactions, which include ionization of the molecule as a first step. The main point is that the electronic structure of a radical cation formed at the initial stage of a reaction determines the reaction path and product composition. Highly reactive radical cations can be produced by ionizing radiation and stabilized in a chemically inert matrix with electron scavenging properties. This simple idea is a basis for the so-called "Freon matrix technique", which has been extensively used for characterization of a large number of hydrocarbon and functional radical cations by electron paramagnetic resonance (EPR) spectroscopy.[1−4] In the case of monofunctional radical cations, ionization typically occurs at the functional group. Meanwhile, to the best of our knowledge, the information on the radical cations with two or more functional groups is limited. Some early results on linear and cyclic radical cations with two functional groups were summarized by Symons.[1] More recent work on related species included the studies of radical cations of vinyl ethers,[5] acrylates,[6] lactones,[7] and heterocycles with two heteroatoms.[8] From a basic point of view, the most interesting case is represented by "bridged" cations produced from bifunctional compounds of general structure X-$(CH_2)_n$-X or X-$(CH_2)_n$-Y (X and Y are functional groups). The species of this kind can be used for investigations of the effects of interaction between functional groups, conformation, and matrix disturbance on spin density and charge distribution, because they should have closely lying electronic states, sensitive to subtle variations. The studies of such effects are important for better understanding of the radiation-induced processes in chemistry and biology and for model purposes in molecular electronics (in view of possible "switching" between the states with different charge distribution). To the best of our knowledge, the information on bridged radical cations was restricted to EPR data for a few simple diethers[1] and optical absorption results for a series of diamines.[9] Systematic studies of the effect of various factors (methylene bridge length, substitution in "bridge" and in functional groups) on the structure and reactivity of radical cations are lacking.

Aliphatic diketones (readily available and widely used in different areas of chemistry) may provide a suitable class of models for the studies of correlation between molecular structure of bridged bifunctional compounds and the properties of ionized species. The radical cations of simple aliphatic ketones are characterized by n_σ-type SOMO localized at the carbonyl oxygen atom.[10,11] We are unaware of any experimental or theoretical works on diketone radical cations. In addition to general modeling, an interesting aspect is concerned with the well-known effect of keto-enolic tautomerism, which makes it possible to characterize both ketonic and enolic forms of radical cations and to follow the peculiarities of their formation and reactivity.

In this work, we have investigated the structure and properties of diketone radical cations using EPR spectroscopy and quantum chemical calculations.

Experimental Section and Calculations

Diketones from Aldrich (2,3-butanedione, 99%; 2,4-pentanedione, 98%; 2,5-hexanedione, 98%; 3-methylpentane-2,4-dione, 85%; 2,3-pentanedione, 98%), Freon-113 ($CFCl_2CF_2Cl$, 99.99%, Galogen, Perm', Russia), Freon-11 ($CFCl_3$, 99.9%, Khimprom, Volgograd, Russia), perfluorocyclohexane, and perfluoro-1,3-dimethylcyclohexane (Pierce, USA) were used as received. Partially deuterated 2,4-pentanedione was synthesized from 2,4-pentanedione and D_2O according to a procedure described elsewhere.[12]

FTIR and NMR spectroscopy were used to check the content of ketonic and enolic forms of the studied substances in freonic solutions. IR spectra were measured with a Bruker Equinox 55S FTIR spectrometer (4000−400 cm^{-1} range, 2 cm^{-1} resolution) and NMR spectra were recorded with Bruker Avance 400 NMR spectrometer.

The freonic solutions of the substances under study (0.05−0.5%) were degassed through a standard freeze−pump−thaw

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10.1021/jp0685380 CCC: $37.00

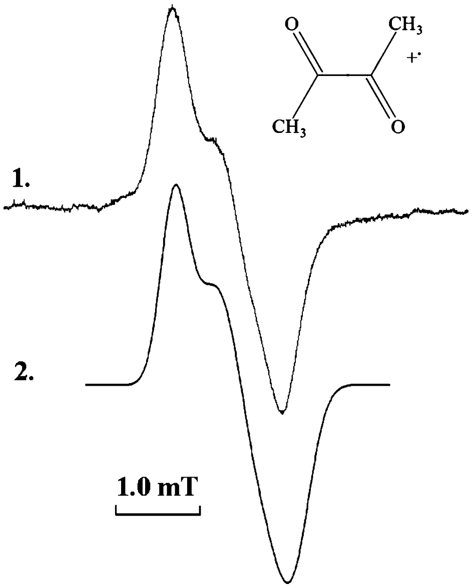

Figure 1. (1) EPR spectrum of the X-irradiated frozen solution of diketone-0 (0.2%) in Freon-113 at 77 K; (2) the best-fit powder simulation for radical cation with g-anisotropy (see text for parameters).

cyclic procedure (typically, three cycles) and irradiated with X-rays (50 keV) at 77 K. The total absorbed dose was in the range of 5−8 kGy. EPR spectra were measured at 77−150 K with an X-band (9.4 GHz) spectrometer with a 100 kHz high-frequency modulation manufactured by SPIN (St. Petersburg, Russia).

EPR spectra of irradiated samples obtained with Freon-11 and Freon-113 were very similar for all the substances studied. For this reason, we present only the results for Freon-113. This glassy matrix was chosen for detailed studies, because it is more suitable for photolysis (better optical quality) and allows one to study the thermally induced ion−molecule reactions of radical cations.[1,3]

Isotropic simulations of the EPR spectra were preformed with a PEST Winsim software, and anisotropic powder simulations were carried out with WINEPR Simfonia (Bruker).

The method of density functional theory (DFT) with Perdew−Burke−Ernzerhof (PBE) and PBE0 exchange-correlation functionals was used for the quantum chemical calculations. As we showed recently, the DFT-PBE approach provides a reasonably good description of the electronic structure and magnetic resonance parameters of complex radical cations; in particular, heterocyclic radical cations with two heteroatoms, which may be considered as bifunctional species.[8] All the DFT calculations were performed using the PRIRODA program package.[13] We used orbital basis sets of contracted Gaussian-type functions of the size (5s1p):[3s1p] for H, (11s6p2d):[4s3p2d] for C, (11s6p2d):[4s3p2d] for N, (11s6p2d):[4s3p2d] for O. In the case of PBE0, the exchange-correlation functional Λ22 and Λ33 basis sets were used.[14] The convergence criterion for the geometry optimizations was set to 1×10^{-5} a.u. for the norm of the gradient, and within each SCF cycle, the convergence criterion was 1×10^{-7} a.u. In questionable cases, energy minima of the optimized molecules have been verified by a calculation of the Hessian. The calculated spin density at the nuclei was converted into isotropic hyperfine coupling constants using formula[15]

$$a_{\mathrm{nuc}}^{\mathrm{iso}} = \frac{4\pi}{3} g_{\mathrm{e}}\beta_{\mathrm{e}} g_{\mathrm{nuc}}\beta_{\mathrm{nuc}} \langle S_z \rangle^{-1} \rho_{\mathrm{nuc}}^{\alpha-\beta}(\delta(r_{\mathrm{nuc}}))$$

Principal values of hyperfine coupling tensor were obtained from principal values of electric field gradient tensor at the nuclei by formula[15]

$$T_{\mathrm{nuc}}(i) = \frac{1}{2} g_{\mathrm{e}}\beta_{\mathrm{e}} g_{\mathrm{nuc}}\beta_{\mathrm{nuc}} \langle S_z \rangle^{-1} E(i)$$

In fact, the anisotropic contribution to hyperfine coupling was found to be significant in only one case (CH proton in the enolic form of 2,4-pentanedione radical cation), so the interpretation and further discussion is based on isotropic hyperfine coupling constants.

All g values of the EPR signals were measured by comparing their position in EPR spectrum with the positions of the reference lines (markers) with known g values produced by Mn^{2+} in MgO powder (the reference sample in the form of thin capillary was placed in resonator together with the studied sample). The values of g factors of third and fourth components of a septet signal from Mn^{2+} were taken as 2.0338 and 1.9810, respectively.

Results

2,3-Butanedione (Diketone-0). Quantum chemical calculations for the radical cation of this diketone give a single stable geometry.

The spin density is mainly located at two oxygen atoms, which corresponds to relatively small isotropic hyperfine coupling constants with all methyl protons (see Table 1). A maximum absolute value of ca. 0.58 mT was found for two protons (one from each methyl group) in a rigid conformation (non-rotating methyl groups). Meanwhile, the average values (assuming fast rotation or pseudo rotation of methyl groups in the EPR time scale) are even much smaller (below 0.03 mT). In any case, most probably, the hyperfine splitting should be unresolved in solid matrices (like for acetone radical cation). In accordance with this expectation, the experimental EPR spectrum (Figure 1) exhibits a broad anisotropic singlet with the total spread of ca. 1.3 mT. The best-fit powder simulation is obtained with the following principal values of g tensor: $g_1 = 2.0067$, $g_2 = 2.0022$, $g_3 = 1.9987$ (curve 2 in Figure 1). These values may be compared with those reported for acetone radical cation: $g_1 = 2.0077$, $g_2 = 2.003$, $g_3 = 2.0019$ (in $\mathrm{CFCl_3}$[16]).

Heating the sample up to 120 K does not result in any noticeable changes in the EPR spectrum, whereas gradual decay of the signal is observed at higher temperatures. Photolysis of the irradiated sample with light in the range of 380−510 nm leads to decrease in the signal intensity without formation of any new paramagnetic species. Slower decay was also observed upon illumination with the light of $\lambda > 510$ nm. In both cases, decay is probably due to ion−electron recombination. Thus, thermal or photostimulated ion−molecule reactions were not observed for this diketone radical cation.

2,4-Pentanedione (Diketone-1). The main difference of this substance from other diketones results from the effect of easy formation of enolic form, which typically predominates over ketonic form in nonpolar solvents[17]

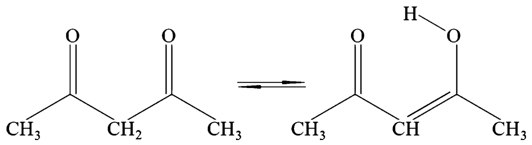

TABLE 1: Comparison of the Calculated and Experimental Isotropic Hyperfine Coupling Constants of the Radical Cations of Diketones

	proton isotropic hyperfine coupling constants (mT)	
radical cation	calcd	exp
2,3-butanedione (diketone-0)	<0.03 (6H)[a] (0.575; −0.321; −0.321)[b]	unresolved
2,4-pentanedione (diketone-1)	ketonic form: ~0.1 (6H, CH_3)[a] (0.012; −0.099; −0.233)[b] 0.1 (2H, CH_2) enolic form: <0.35 (6H, CH_3)[a] (−0.041; 0.537; 0.531)[b] 1.97 (1H, CH) 0.36 (1H, OH)	unresolved (ketonic form); 1.92 (1H, enolic form)
3-methylpentane-2,4-dione (diketone-1-CH_3)	ketonic form: 0.14 (6H, CH_3CO-)[a] (−0.205; −0.115; −0.092)[b] 0.48 (1H, CH) 0.35 (3H, “bridge” CH_3)[a] (0.522; −0.002; 0.521)[b] enolic form: <0.3 (6H, CH_3CO-)[a] (0.482; −0.072; 0.482)[b] 0.34 (1H, OH) 2.69 (3H, “bridge” CH_3)[a] (4.046; 0.020; 3.990)[b]	2.65 (3H, enolic form)
2,5-hexanedione (diketone-2)	0 (6H, CH_3) (−0.146; 0.268; −0.136)[a] 0.52 (2H, CH_2) 0.26 (2H, CH_2)	0.67 (2H)
2,3-pentanedione (ethyl-methyl-diketone-0)	0.24 (3H, CH_3 in ethyl)[a] (0.025; 0.515; 0.078)[b] <0.03 (3H, CH_3CO-)[a] (0.528; −0.305; −0.318)[b] 0.30 (2H, CH_2)	unresolved

[a] Averaged hyperfine coupling constants for the methyl protons. [b] Values for rigid structure with non-rotating methyl groups.

Relative abundance of the two forms in solution of diketone-1 in Freon-113 was evaluated by FTIR and NMR spectroscopy. IR spectrum exhibits an intense characteristic band of enolic form at 1618 cm^{-1}, whereas the carbonyl stretching feature of ketonic form (1709 cm^{-1}) is quite weak. The NMR spectrum shows strong signal from enolic form (15.54 ppm, the enolic proton at the oxygen atom) and a much weaker feature of ketone (3.53 ppm, methylene “bridge” protons). As follows from integrated intensities of the NMR signals, the ratio of ketonic to enolic form is ca. 1:9. We may assume that this ratio does not change much for a glassy solid formed by rapid freezing of the freonic solution.

According to the quantum chemical calculations, there are two stable conformers of the radical cation of the ketonic form with the difference in energy of about 7 kcal/mol. In the lower-energy state, the spin density distribution again corresponds to a n_σ(O)-type structure with very small hyperfine coupling constants for all protons (maximum 0.1 mT, if we assume dynamical averaging of methyl protons, or 0.2 mT for rigid structure), whereas the second state exhibits relatively large coupling constants for two methylene protons (0.77 and 0.76 mT).

The enolic form of the radical cation has six stable conformers (the structures differing by only a 60° rotation of a methylene group around the C−C bond with an energy difference of less than 0.5 kcal/mol were considered as being one conformer). The most favorable conformer of the enolic-type radical cation lays 19.6 kcal/mol below the lowest-energy ketonic form. It exhibits a slightly asymmetrical pseudocyclic structure (Figure 2) with substantial separation of charge and spin. Major spin density in this distonic-type radical cation is located at the bridge carbon atom. The calculated isotropic hyperfine coupling constant for the bridge proton is 1.97 mT, which is typical for α-protons in carbon-centered π-electron radicals. Experimental EPR spectrum in Freon-113 or Freon-11 (curve 1 in Figure 2) shows a strongly asymmetrical doublet pattern. It is worth noting that this signal cannot originate from a single species, because it is impossible to simulate its line shape and relative intensity of the components even assuming the anisotropy of both hyperfine coupling and g tensor. On the other hand, the signal can be interpreted as a superposition of a broad singlet with $g_{av} = 2.012$ and a doublet with $a(^1H) = 1.92$ mT and $g_{av} = 2.0054$ (curve 2 in Figure 2). The best-fit simulation yields the 1:5 ratio of integrated intensities of singlet to doublet signal. An additional proof for this interpretation was obtained by heating the sample to 120 K, which leads to reversible separation of the two EPR signals due to line narrowing (curve 3 in Figure 2). The doublet signal (which exhibits narrower lines at 120 K) definitely results from the enolic form of the radical cation, in excellent agreement with the DFT calculations. The most logical interpretation of the singlet signal is its assignment to the lowest-energy ketonic form of the radical cation with very small calculated proton couplings. However, this assignment encounters the problem of unusually large positive g shift, so we have to consider additional experimental arguments. First, we can exclude the role of impurities in matrix or studied compound, because the purity of diketone-1 was additionally checked by NMR and the result is completely reproducible in two different matrices (Freon-113 and Freon-11). Second, we have studied the effect of deuteration on the EPR spectrum. The spectrum

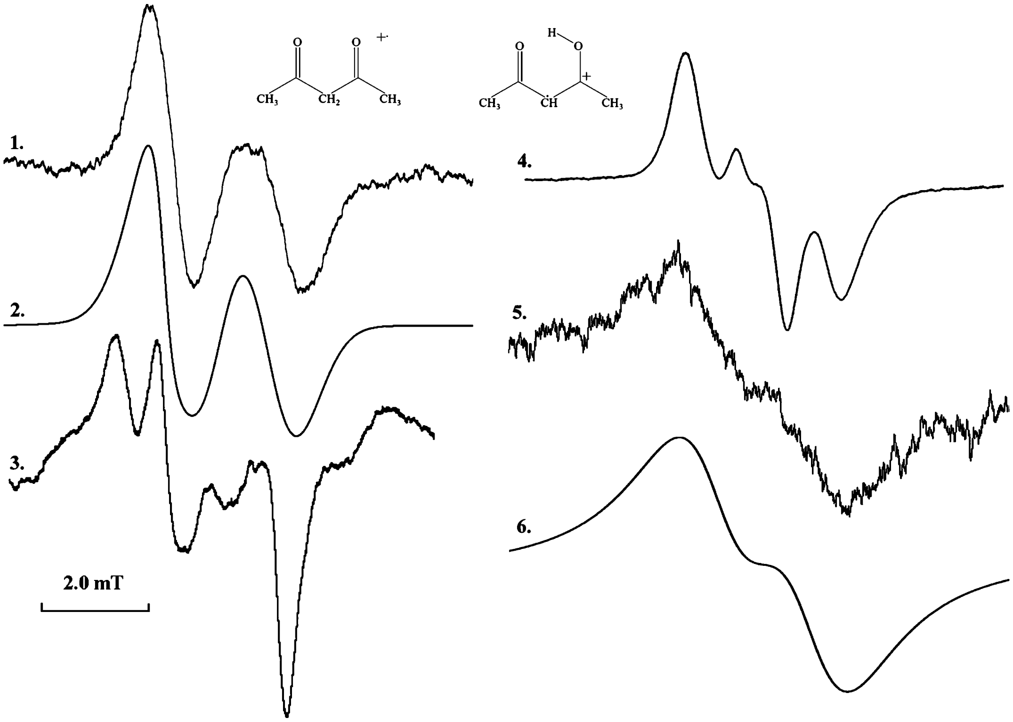

Figure 2. EPR spectra of X-irradiated frozen solutions if not stated otherwise: (1) diketone-1 (0.2%) in Freon-113 at 77 K; (2) best-fit isotropic simulated EPR spectrum of the 1:5 mixture of ketonic and enolic forms of the radical cation (0.984 correlation coefficient, see text for parameters); (3) diketone-1 (0.2%) in Freon-113 at 120 K; (4) mixture of diketone-1-d$_x$ and diketone-1 (totally 0.5%) in Freon-113 at 77 K; (5) diketone-1 (0.5%) in perfluorocyclohexane at 77 K; (6) isotropic simulation of the EPR spectrum of enolic form of the radical cation with large line width.

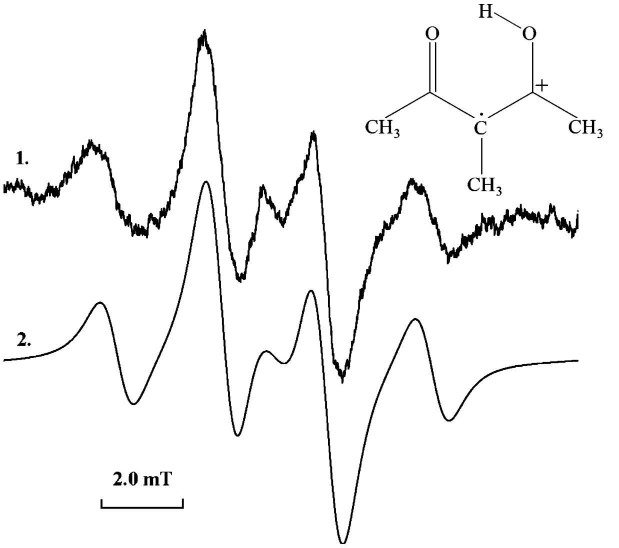

Figure 3. (1) EPR spectrum of the X-irradiated frozen solution of diketone-1-CH$_3$ (0.2%) in Freon-113 at 77 K; (2) the best-fit isotropic simulated EPR spectrum of enolic radical cation (see text) plus ca. 15% of singlet signal with the same *g* value (0.978 correlation coefficient).

produced from partially deuterated diketone-1 (ca. 50% of deuteration) can be represented as a mixture of three signals: singlet with high *g* value, doublet with $a(1H) = 1.92$ mT (both observed in non-deuterated sample) and an additional singlet with exactly the same *g* value as for the doublet signal (Figure 2, curve 4). A new singlet signal is actually an unresolved triplet resulting from enolic radical cation with deuterium instead of H at the bridge carbon atom (taking into account the ratio of $a_H/a_D = 6.51$). We should note that deuteration has no effect on the low-field singlet with high *g* value, which is in accord with its assignment to a species with no measurable proton splitting.

Additional experiments were made with nonpolar perfluorinated matrices. Despite the fact that the EPR spectra obtained in these matrices were strongly broadened and somewhat noisy, common trend appears to be evident. In the case of perfluoro-1,3-dimethylcyclohexane matrix, the relative contribution of the doublet signal becomes larger than that in Freons. Taking perfluorocyclohexane as a matrix results in an almost symmetrical, very broad doublet EPR signal (curve 5 in Figure 2), which may be assigned to a pure enolic form of the radical cation. Detailed consideration of these matrix effects and further arguments for spectral assignment will be given in the Discussion section.

Photolysis at $\lambda > 420$ nm results in only a slight decrease of the integrated intensity of the signal and heating the sample leads to reversible narrowing of the spectral lines. Thus, there is no evidence for thermal or photochemical reactions of the radical cations in ketonic or enolic form.

3-Methylpentane-2,4-dione (Diketone-1-CH$_3$). The IR spectrum of this diketone in Freon-113 shows the presence of both ketonic and enolic forms. The relative abundance of the two forms is almost equal (1:1), as revealed by NMR data (the signals at 16.45 ppm for the enolic proton at the oxygen atom and 3.67 ppm for the bridge CH proton of the ketonic form).

Three unique geometries of the ketonic form of radical cation were obtained by quantum chemical calculations. The relative energies of two unfavorable conformers are 8.42 and 10.18 kcal/mol, respectively. According to calculations (see table), all the proton isotropic hyperfine constants in the most favorable conformer are below 0.5 mT, so the EPR spectrum of this species should be an unresolved singlet if the line width is larger than 0.5 mT. Two other conformers of the ketonic form should yield quartet signals with $a(3H) = 0.55$ and 0.86 mT, respectively.

The enolic form of radical cation is represented by three conformers. The most favorable one is, in fact, a carbon-centered distonic-type radical, similar to enolic form of diketone-1. The total energy of the radical cation of this conformer is lower than that of the most stable ketonic form by 16.50 kcal/mol. In this case, major hyperfine coupling results form the protons of methyl group attached to the bridge carbon, which should lead to a quartet signal with a splitting of 2.69 mT (dynamically averaged, very close to that for methyl β-protons in ethyl radical).

The experimental EPR spectrum is shown in Figure 3. The main component of this spectrum is a relatively broad binomial quartet signal centered at $g = 2.0045$ with the hyperfine splitting of 2.65 mT, which perfectly matches the theoretical prediction for enolic form of the radical cation. In addition, one can see a small singlet signal in the center of experimental spectrum. At first glance, it might be a signal from the ketonic form. However, the g factor of the singlet is almost the same as that of the signal from enolic form, which is in contrast with marked difference between ketonic and enolic forms of the radical cation for unsubstituted diketone-1. Thus, most likely, the singlet signal originates from some impurity. If the signal from the ketonic form of the radical cation of diketone-1-CH_3 has the same g value as for diketone-1 (2.012), the corresponding signal would overlap with the second line of quartet from enolic form. Meanwhile, there is no significant distortion of this component of quartet, which means that the contribution from the ketonic form of the radical cation is negligible.

Photolysis with $\lambda > 510$ nm does not lead to any significant spectrum changes. Increasing the temperature results in reversible narrowing of the lines in the EPR spectrum. Thus, just like in the case of diketone-1, we see no distinct signs of thermal or photochemical reactions.

2,5-Hexanedione (Diketone-2). This diketone exists only in ketonic form, as confirmed by IR spectrum of its solution in Freon-113, which exhibits only the carbonyl stretching band at 1722 cm^{-1}.

Quantum chemical calculations for the radical cation of diketone-2 revealed eight stable conformers with a total energy difference within 12 kcal/mol. The calculated hyperfine coupling constants for the most favorable conformer are given in the table. All other calculated conformations have the proton isotropic coupling constants below 0.87 mT. The experimental spectrum exhibits a slightly asymmetrical triplet pattern with $g_{av} = 2.0032$ (close to that of diketone-0, but with smaller g anisotropy) and hyperfine splitting of ca. 0.67 mT in reasonable agreement with theory.

Heating the sample results in slow transformation of the initial signal into a broadened triplet with ca. 2.0 mT hyperfine splitting, which remains incomplete even at 155 K. The resulting signal should originate from intermolecular proton transfer from radical cation to a neutral molecule, which typically occurs in a Freon-113 matrix above 105−110 K.[4] In fact, there are two possible structures, which may be consistent with the observed EPR spectrum. The first one corresponds to deprotonation from a "bridge" methylene group yielding a $CH_3CO^{\bullet}CHCH_2COCH_3$ radical. Such a radical can yield a roughly triplet spectrum, only if we assume the conformation with 2.0 mT splitting from one α and one β-proton, whereas the other β-proton has a splitting much smaller than 1.0 mT. According to quantum chemical calculations such a geometry (it was initially chosen according to the "$\cos^2 \theta$ rule") is not the most favorable one. However, it lies only 1.0 kcal/mol above the lowest-energy conformer, so its stabilization is possible because of matrix effects. Another possibility is deprotonation from the methyl group yielding the radical of the structure $CH_2COCH_2CH_2COCH_3$, which should give a roughly binomial triplet EPR spectrum. The calculations give the isotropic hyperfine coupling constants of ca. 2.16 mT for α-protons in this radical. The energy of such radical is 4.59 kcal/mol higher than the most favorable conformer of the radical with radical center on the bridge.

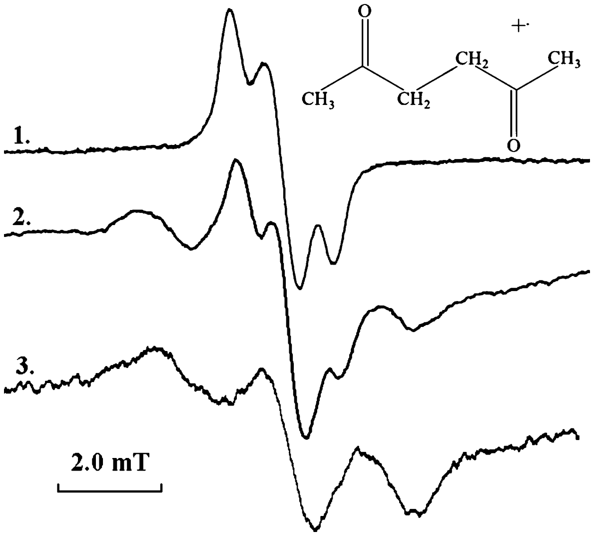

Figure 4. (1) EPR spectrum of the X-irradiated frozen solution of diketone-2 (0.2%) in Freon-113 at 77 K; (2) EPR spectrum of the sample after ∼3 min annealing at 140 K, (3) the same sample after photolysis with the light of $\lambda = 380-460$ nm for 7 min.

Photolysis at $\lambda > 510$ nm light (15 min) results in a slow decrease of the signal intensity without formation of any new paramagnetic species. Meanwhile, irradiation with the light of $\lambda = 380-460$ nm (7 min) leads to the same transformation as heating the sample. Most probably, the structure of radical center is the same as in deprotonation product; however, the mechanism of transformation is not fully clear. In particular, this may be an intramolecular proton-transfer giving a distonic-type carbon-centered radical cation, which should have virtually the same magnetic parameters as the corresponding neutral radical.

2,3-Pentanedione (Ethyl-methyl-diketone-0). Quantum chemical calculations of the radical cation of this non-symmetrical diketone revealed two possible conformers, which differ in total energy by only 1.09 kcal/mol. In the lowest-energy case, the largest hyperfine coupling is 0.63 mT (see table). The other conformer has even smaller hyperfine constants (maximum 0.32 mT). Thus, most probably the corresponding splittings should be unresolved. Indeed, experiment reveals a broad, slightly asymmetrical singlet signal with $g_{av} = 2.0018$ and the total observed line width of 1.5 mT (Figure 5). This signal is rather similar to that observed for a symmetrical dimethyl diketone (diketone-0) with the only difference being that g components are unresolved for the ethyl derivative, which may be due to larger line broadening resulting from unresolved hyperfine coupling from methylene protons.

Heating the sample above 110 K results in the appearance of the binomial-like quintet signal with main splitting of a(4H) ≈ 2.20 mT and additional substructure. The most logical assumption is that this signal results from a neutral radical $CH_3^{\bullet}CHCOCOCH_3$, which corresponds to deprotonation of the radical cation at the methylene group. In this case, the α-proton and the β-protons are nearly magnetically equivalent, which is typical for $CH_3^{\bullet}CHX$ radicals. The signal shape exhibiting some "substructure" of the signal can be explained by anisotropy of hyperfine coupling with α-protons and incomplete equivalence of α- and β-protons.

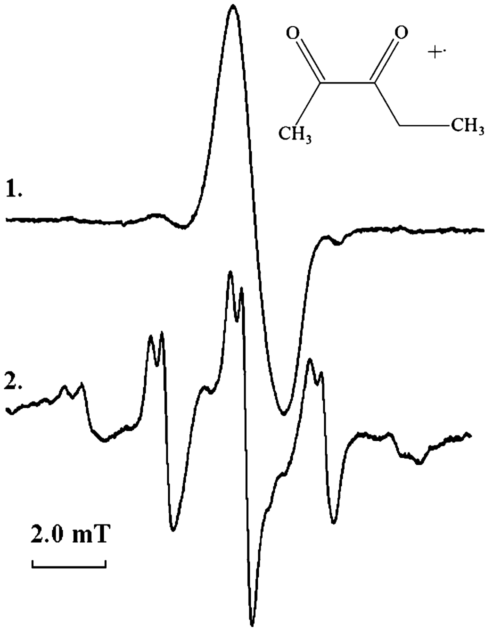

Figure 5. (1) EPR spectrum of the X-irradiated frozen solution of ethyl-methyl-diketone-0 (0.5%) in Freon-113 at 77 K; (2) the same sample measured at 77 K after heating to 145 K.

Photolysis of the irradiated sample leads to a complex, poorly resolved pattern, which can be interpreted tentatively as a superposition of signals from radical cations and neutral radicals.

Discussion

Both experimental and calculation results obtained in this work show that the ketonic forms of diketone radical cations containing up to two bridge methylene groups have a symmetrically delocalized structure with major spin population at two carbonyl oxygen atoms. Because these radical cations are characterized by an n_σ-type SOMO, the hyperfine interaction between unpaired electron and protons is weak and the corresponding coupling constants are small (in fact, resolved hyperfine splitting in the EPR spectrum was obtained only for diketone-2 radical cation).

In the cases of diketone-0, diketone-2, and ethyl-methyl-diketone-0, interpretation is quite clear, whereas assignment of the ketonic form of the diketone-1 radical cation presents a specific problem because of the unexpectedly large positive *g* shift (as compared with the free electron value g_e). The observed *g* value for this radical cation (2.012) is substantially higher than the corresponding values for other ketone radical cations (acetone, diketone-0, diketone-2) and can be compared, for example, with those for oxygen-centered ether radical cations.[18] First of all, we should clarify the interpretation of the experimental EPR spectrum for diketone-1 in view of all the results obtained in this work. As shown above, the results obtained for partially deuterated diketone-1 clearly reveal two signals from the enolic form (doublet and the singlet with the same *g* factor) and one singlet signal with a substantially larger *g* factor. As the impurity effect can be neglected (see above), one should admit that the latter singlet belongs to product of ionization of diketone-1, which is insensitive to deuteration. This means that it could be only an oxygen-centered radical or a classic radical cation (not a distonic isomer), which has only very small proton hyperfine coupling constants. Now we can consider the matrix effect on the ratio of two radical cations. It is well-known that the keto-enolic tautomeric equilibrium is very sensitive to solvent polarity.[19] The experimental value of the enol to ketone ratio in a low-polar Freon-113 solution obtained by NMR lies between those reported for THF (7.2) and toluene (10). Extremely polar solvents (like water) dramatically shift the equilibrium toward ketonic form; however, it is impossible to use such matrices because of fast deprotonation of initial radical cations. In the other extreme case, a nonpolar solvent such as cyclohexane, the equilibrium constant is as large as 42, which means that the equilibrium concentration of ketonic form in dilute solutions becomes negligible. Similar effects should be expected for nonpolar perfluorinated hydrocarbons, which can be used as matrices for trapping of radical cations. Indeed, taking perfluorinated 1,3-dimethylcyclohexane (less polar than Freon) and cyclohexane (nonpolar) as matrices, we have obtained a definite decrease in the relative abundance of singlet signal with a high *g* value in the EPR spectrum (see above). Thus, there is a correlation between relative intensity of singlet signal in irradiated frozen matrix and concentration of ketonic form in a liquid solution. In our view, this correlation proves our assumption that the keto-enolic equilibrium is not shifted much upon rapid freezing of the solutions and supports the assignment of the singlet with a high *g* value to the ketonic form of the radical cation. Indeed, in a nonpolar perfluorocyclohexane matrix, we see only the signal from the enolic form radical cation, because concentration of the ketonic form prior to ionization is too low.

Thus, from an experimental point of view, we have to conclude reasonably that the singlet with a large *g* factor should belong to the radical cation of the ketonic form of diketone-1. However, the theoretical interpretation of this result is not straightforward. A relatively large *g* value means a significant contribution of orbital magnetism due to “defreezing” of angular momentum (typical for many oxygen-centered radicals and radical cations, but not for known ketonic radical cations). This may imply the presence of closely lying electronically excited states in diketone-1 radical cation that do not occur in other ketone radical cations. Unfortunately, poor resolution of the EPR spectra does not allow us to determine the components of the *g* tensor, which makes detailed analysis impossible. Elucidation of the peculiarities of electronic structure of the diketone-1 radical cation would require further experimental and theoretical efforts, including optical absorption studies, experiments with high degree of isotopic substitution, and more demanding calculations of excited states. At this stage, we will stay with preliminary phenomenological conclusion.

It is worth noting that the radical cations of diketone-0 and diketone-1 (in ketonic form) exhibit remarkable thermal and photochemical stability, and the radical cation of diketone-2 shows very slow and incomplete deprotonation at relatively high temperatures (140 K and above). It is well-known that many organic radical cations undergo ion−molecular reaction with parent-neutral molecules (proton transfer) in a Freon-113 matrix when the samples is heated to ca. 110 K.[1−4] The absence of this reaction may be explained by relatively low acidity of the radical cations of diketones (the acidity of specific protons in radical cations is supposed to correlate with hyperfine coupling constant for these protons[1]). However, radical cations of ethyl-methyl-diketone-0 undergo deprotonation at specific positions, which may indicate significance of other factors.

Radical cations of the enolic forms show a π-type structure (in agreement with the data of photoelectron spectroscopy[20,21]) and their magnetic parameters were found to be in very good agreement with calculations. These distonic-type species are thermodynamically stable, so they do not show any thermal reactions in a Freon-113 matrix.

The studies of radical cations of diketone-1 and its methylated analogue (diketone-1-CH_3) reveal a marked difference between the ratio of ketonic and enolic forms in neutral and ionized states. This result indicates selection upon ionization or preferential stabilization of a specific ionic form. The effect is very strong in the case of diketone-1-CH_3, where only the enolic form of the radical cation was identified reliably after irradiation in a Freon-113 matrix. As mentioned above, ketonic and enolic forms of parent neutral molecules are present in the freonic solution in nearly equal concentrations, so there are two possible explanations of this effect: selection of the enolic form in the process of positive charge transfer or transformation of the ketonic form of the radical cation to a more stable enolic form due to intramolecular H atom transfer occurring after ionization. In the first case, one should consider ionization potentials (IP) of the two forms. The reported experimental vertical IP values for ketonic and enolic forms of this diketone are 9.43 and 8.55 eV, respectively.[20] In reasonable agreement with this data, our calculations give vertical IP values of 9.15 (ketone) and 8.47 eV (enol). Thus, the IP difference is rather large (ca. 0.7−0.9 eV), which provides enough driving force for positive hole transfer between these two forms (denoted as K and E)

$$K^{+\bullet} + E \rightarrow E^{+\bullet} + K$$

An effective distant trap-to-trap positive hole transfer between organic molecules in frozen freonic matrices (most probably, a single-step tunneling) was found previously.[22−24] This mechanism is operative at the distances of ca. 2−3 nm (i. e., just in the range of concentrations used in this work) provided that $\Delta IP > 0.3$ eV.[24] The second opportunity (transformation of $K^{+\cdot}$ to $E^{+\cdot}$ due to intramolecular H transfer in the ionized state) also cannot be excluded, because it is favorable from a thermodynamic point of view by 16.5 kcal/mol. However, we have to note that such a reaction may be kinetically unfavorable in a rigid Freon matrix at 77 K. Indeed, the ketonic form of radical cation is stable under similar conditions in the case of unsubstituted diketone-1, even though its calculated energy is higher than that of the enolic form by 19.6 kcal/mol.

Preferential stabilization of the thermodynamically less favorable ketonic form of radical cation in the case of diketone-1 looks somewhat surprising. The preference is not strong, but still substantial. A tentative explanation again can be related to positive hole transfer between different forms. The reported experimental vertical IP values for the enolic form lie between 9.0 and 9.2 eV,[20,21,25] whereas the value of 9.6 eV was reported for the ketonic form.[20] Meanwhile, our calculations provide almost equal IP (vert.) values for both forms: 9.35 and 9.31 eV for ketone and enol, respectively. Despite some uncertainty, we may assume that the IP difference between two forms of diketone-1 is relatively small (substantially smaller than for diketone-1-CH_3). In such cases, the gas-phase IP values are no more good guides for determination of the efficiency and direction of the positive hole transfer in solid matrices. The environment effects become crucial, which may result in selection of specific conformers or even inversion of the direction of hole transfer upon changing matrix.[23,24] The ionization potentials of molecules in solid phase are lower than those in the gas phase because of polarization of the medium. If we assume that the radical cations of ketonic form stronger interact with environment, their IP values should decrease to a larger extent when going from gas phase to condensed phase. The difference should not be large, but in the case of close IPs, this may be enough to interchange the relative positions of the ionization energies of the two forms. Therefore, we may suggest tentatively that some preference in stabilization of the ketonic form for diketone-1 ($[K^{+\cdot}]/[E^{+\cdot}] > [K]/[E]$) can be attributed to partial positive hole transfer from $E^{+\cdot}$ to K, which becomes possible because of the matrix effect (that is, stronger stabilization of the ketonic form of radical cation by environment).

To test the role of distant positive hole transfer between different molecular forms in the systems under study, we have carried out an additional experiment with the irradiated frozen freonic solution of a 1:1 mixture of diketone-1 and diketone-1-CH_3. In the absence of trap-to-trap hole transfer, one should expect an additive EPR spectrum (that is, a superposition of the spectra observed for individual substances). Meanwhile, the experimental spectrum shows major contribution from the quartet signal resulting from the enolic form of diketone-1-CH_3. This result clearly indicates positive hole migration to the species with the lowest ionization energy, because the enolic form of diketone-1-CH_3 has the lowest IP much lower among the four main forms of the solute molecules.

Conclusions

We have obtained the EPR spectra of ketonic and enolic forms of a number of diketone radical cations. The ketonic forms exhibit major spin population at two oxygen atoms and small proton hyperfine coupling constants, whereas the enolic forms resemble carbon-centered π-electron radicals with characteristic hyperfine coupling to α- and β-protons. To the best of our knowledge, the EPR spectra of the enolic-type radical cations were characterized for the first time. All the experimental results are in good agreement with DFT calculations. Diketone radical cations were found to be less reactive than the radical cations of many other functional organic cations, presumably due to delocalization of charge and spin density and relatively low acidity of specific protons An interesting effect revealed in this work is the selection of specific forms of diketone (enolic or ketonic) upon ionization in solid matrix. In particular, in the case of diketone-1-CH_3, the enolic form of the radical cation strongly predominates after irradiation of the frozen matrix despite the fact that both forms are present in nearly equal concentrations in the liquid solution. The effect was attributed tentatively to the positive hole transfer between different forms occurring in rigid matrix after ionization. In our view, further studies of selection of specific molecular forms (isomers or conformers) upon ionization in rigid matrices may shed light on basic issues of radiation-induced processes in molecular solids, polymers, and biologically important systems.

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (Project 06-03-33104).

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