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Delocalized methoxyacetone radical cation: structure and reactivity

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The radical cation (RC) of methoxyacetone exhibits a delocalization of spin density between two oxygen atoms with considerable spin population on methylene hydrogen atoms, which results in the selective deprotonation of this RC.

The radical cations (RCs) of bifunctional compounds like $X–(CH_2)_n–Y$ (X and Y are functional groups) are of considerable interest as model systems in molecular electronics, the radiation chemistry of macromolecules and radiobiology. Meanwhile, the studies of the structure and properties of these species are limited.[1–3] Recently, we showed that, in a diketone RC (X = Y = MeCO), the spin density was distributed equally on both keto groups,[4] whereas for amidoester radical cations ($X = CONMe_2$, Y = MeOCO) spin populates mostly the amide moiety,[5] regardless of the bridge length (n = 0–4). Apparently, the driving force for this localization is difference between the ionization potentials (IPs) of functional groups X and Y, which is large enough for amidoesters (ΔIP_{XY} ~ 1 eV) to ignore any possible matrix effect. Here, we report the study of a 'bridged' bifunctional system with X = MeO, Y = MeCO, which has much smaller ΔIP_{XY} (~0.33 eV as evaluated from a comparison of dimethyl ether and acetone[6]). The radical cation of methoxyacetone (n = 1) was generated by X-irradiation of the frozen solutions of the corresponding substance (0.5 vol%) in Freon 113 ($CF_2ClCFCl_2$) and Freon 11 ($CFCl_3$) at 77 K. The EPR studies were complemented by a theoretical DFT analysis (PBE functional[7] with orbital basis sets of contracted Gaussian-type functions of the size (5*s*1*p*):[3*s*1*p*] for H, (11*s*6*p*2*d*):[4*s*3*p*2*d*] for C, (11*s*6*p*2*d*):[4*s*3*p*2*d*] for O, PRIRODA computational program[8,9]).

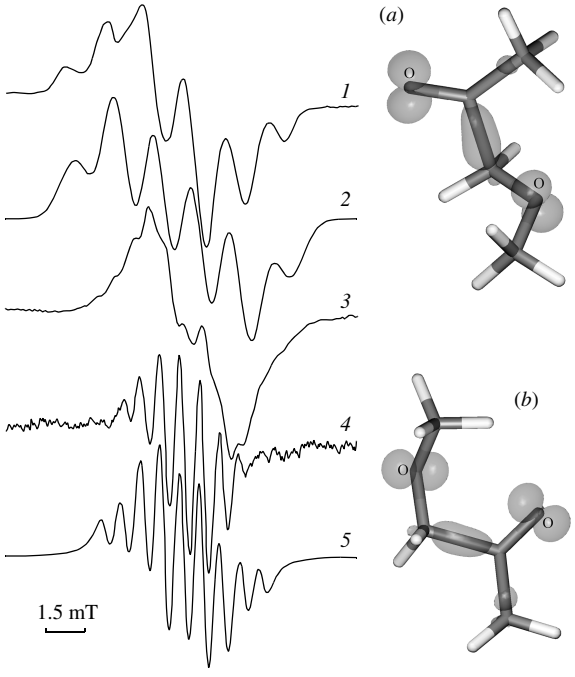

Figure 1 (*1*) Experimental EPR spectrum of X-irradiated methoxyacetone in Freon 113 at 77 K; (*2*) isotropic simulation, a doublet of quartets; (*3*) the same as (*1*) after heating up to 145 K; (*4*) experimental EPR spectrum of X-irradiated methoxyacetone in Freon 11 at 77 K; (*5*) isotropic simulation, a quartet of triplets. Calculated spin density distribution in the radical cation of methoxyacetone: (*a*) higher energy conformation and (*b*) the lowest energy conformation.

The EPR spectrum of the methoxyacetone RC in a Freon 113 matrix at 77 K (Figure 1) can be interpreted as a doublet of quartets with a(1H) = 2.3 and a(3H) = 1.2 mT. It is clear that the larger coupling constant is due to one methylene proton and the quartet results from three equivalent protons of the methoxy group. The calculations yield two conformers (ΔE = 1.71 kcal mol^{-1}) with the spin population divided almost equally between oxygen atoms. One of these conformers with a slightly higher population of carbonyl oxygen (37.9 *vs.* 31.8%) gives the calculated coupling constants a(1H) = 2.57 and a(3H) = 1.31 mT, which match well the experimental data. The second methylene proton gives a small coupling constant (calculated: 0.07 mT), and it is unresolved in the experiment. As expected, the methyl group protons attached to carbonyl are not seen because of very small coupling constants (similar to the case of an acetone RC[10]). The coupling constants for methoxy protons look quite reasonable in comparison with a(6H) = 4.3 mT in a dimethyl ether RC,[11] taking into account that the spin population at the ether oxygen in a methoxyacetone radical cation is approximately one-third of that in a dimethyl ether RC.

It is well known that RCs undergo deprotonation due to an ion–molecule reaction with parent neutrals occurring in a Freon 113 matrix due to diffusion starting at *ca.* 110 K and the proton loss is highly selective, correlating with the maximum spin density position.[12–14] In other words, the most acidic proton in an RC has the largest hyperfine coupling constant. In accordance with this rule, the methoxyacetone RC shows deprotonation from the methylene bridge in this matrix. Spectrum *3* in Figure 1 may be interpreted as a doublet with a(1H) ~ 1.3 mT and additional multiplet subsplitting of 0.4–0.5 mT (poor resolution prevents us from more accurate determination). The calculations yield a(1H) = 1.311, a(3H-ether) = 0.47 and a(3H-carbonyl) = 0.31 mT for the MeOC·HCOMe radical.

Using Freon 11 as a matrix gives another spectrum of smaller total spread (Figure 1), which can be interpreted as a quartet of triplets with a(3H) = 1.57 and a(2H) = 0.75 mT. In this case, two equivalent bridge protons have the same dihedral angle θ close to 60° relative to the axis of the unpaired

electron orbital (in accordance with a well-known semi-empirical $\cos^2\theta$ rule for the hyperfine coupling constants for β-protons: $a \approx B\rho\cos^2\theta$, where $B = 9.0$ mT for the O-centered π-type RC[12]). The experimental spin population on the ether oxygen atom is about 34.9%, as was derived from experimental hyperfine coupling constants using the above $\cos^2\theta$ rule (calculated: 33.54%). Nevertheless, the geometry is somewhat different from the theoretical one (the theory predicts nonequivalent methylene protons, $\theta = 45°$ and 81°, and calculated hyperfine coupling constants of 1.77 and 0.52 mT, respectively). This could be explained by a disturbance of the RC geometry in a Freon matrix (15–20° turn around C–C bond). The selective stabilization of different RC conformers in Freons 11 and 113 was observed previously for a number of RCs.[13,15,16] Probably, it is determined by different matrix microstructure. Since the RC conformation defines the spin density distribution, this could result in different paths of ion–molecule reactions. However, in a polycrystalline matrix of Freon 11, ion–molecule reactions normally do not occur at temperatures up to ~155 K.

In conclusion, we have shown that a methoxyacetone RC has a delocalized structure with an extensive distribution of spin population between two functional groups. This observation supports a rough criterion on delocalization in a non-symmetrical bridged bifunctional RC: a delocalized structure may be expected if ΔIP_{XY} is ~0.3–0.4 eV; that is, the delocalization may occur if the difference in the ionization potentials is comparable with possible matrix effects. The deprotonation of delocalized methoxyacetone RCs occurs at a maximum spin density position.

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