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IR-spectroscopic manifestation of the diacetyl radical anion produced by irradiation of diacetyl in a dimethyl ether matrix at 7 K

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The strongest vibrational feature of a radical anion produced from the diacetyl molecule under radiolysis in a low-temperature dimethyl ether matrix has been characterized for the first time by the analysis of IR- and EPR-spectroscopic data supported by quantum-chemical calculations.

Unstable radical anions produced by electron attachment to organic molecules are key reactive intermediates in various chemical processes, in particular, in radiation chemistry and radiobiology.[1,2] These species were characterized by EPR and UV-VIS optical absorption spectroscopy using the radiation-induced generation of excess electrons in low-temperature glassy molecular matrices (frozen solutions of hydrocarbons, ethers, or alcohols) doped with test compounds.[3,4] Under the radiolysis of such matrices, a primary matrix radical cation reacts with a neutral matrix molecule forming a radical and a protonated ion, while the electron can be trapped by a scavenger to yield a corresponding radical anion. Recently,[5–7] we applied this method to the EPR studies of radical anions produced from bifunctional carbonyl compounds in a diethyl ether matrix at 77 K. Meanwhile, little is known on the vibrational spectra of unstable aliphatic radical anions. Such data closely related to characteristics of chemical bonding are of interest; however, they can be hardly obtained under the radiolysis of frozen solutions. Here we report the first example of IR-spectroscopic characterization of an unstable aliphatic carbonyl radical anion produced by a radiation-chemical method from the diacetyl molecule in a low-temperature deposited dimethyl ether matrix.

We used diacetyl in a dimethyl ether matrix as a model system because diacetyl affords radical anions with a characteristic EPR spectrum in different matrices[5,8–10] and dimethyl ether gives a simple EPR spectral pattern of the radical produced from its radiolysis. Furthermore, it provides a relatively wide spectral window for IR measurements, as compared to more complex organic molecular matrices. The identification was based on a correlation between EPR- and IR-spectroscopic data and their agreement with quantum-chemical calculations, following the approach developed for the assignment of the IR spectra of radiation-induced radicals in noble-gas matrices.[†,11,12]

The EPR spectrum of pure irradiated dimethyl ether at 9–50 K reveals an anisotropic broad triplet signal with the hyperfine coupling constant a_{2H} = 2.0±0.1 mT attributed to the $^{\bullet}CH_2OMe$ radical. Irradiation of the deposited diacetyl/dimethyl ether mixture (1:200) leads to the appearance of the above-mentioned broad triplet signal superimposed with a sharper multiplet signal with an observed splitting of $a \approx 0.7$ mT, the latter being low-field shifted [Figure 1(*a*)]. Although the outer components of this multiplet are hidden by the broad signal components from the $^{\bullet}CH_2OMe$ radical, it is reasonable to assign it to the diacetyl radical anion known in other matrices (septet with a = 0.6–0.7 mT[8–10]). The experiment with an additional electron scavenger (Freon 11) gives further support to this interpretation. Freon 11 is known to scavenge excess electrons giving the $^{\bullet}CFCl_2$ radical, which yields

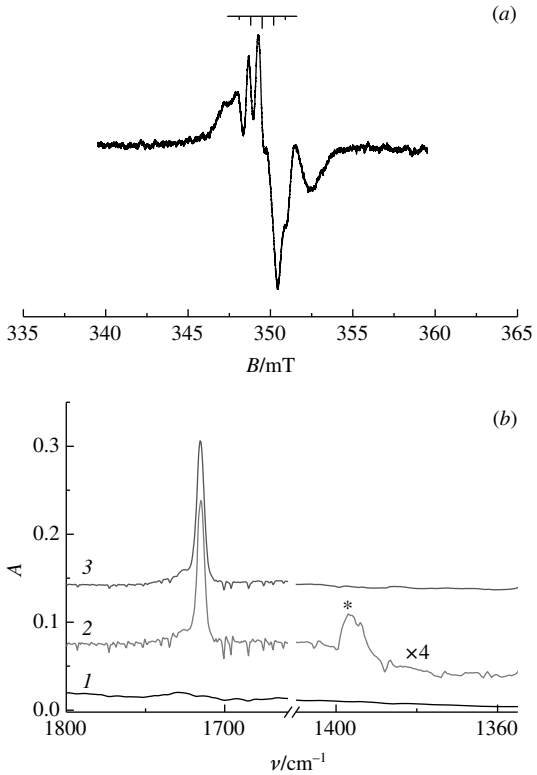

Figure 1 (*a*) EPR spectrum of the irradiated deposited diacetyl/dimethyl ether mixture (1:200) recorded at 50 K; (*b*) IR spectra of the irradiated deposited samples recorded at 7.5 K: (*1*) neat dimethyl ether; (*2*) diacetyl/dimethyl ether (1:200); (*3*) Freon 11/diacetyl/dimethyl ether mixture (1:2:200).

† The experimental procedure based on a matrix deposition technique was described in detail elsewhere.[12] Diacetyl (butanedione-2,3, Fluka, ⩾ 99.0%), dimethyl ether (Me_2O, Aldrich, ⩾ 99%), and Freon 11 ($CFCl_3$, Volgograd AO Khimprom, Russia, 99.9%) were used as received. The gaseous mixtures of known composition were deposited at 50 K onto a cooled KBr plate (in the IR cryostat) or a sapphire rod (in the EPR cryostat). The samples were cooled to 7.5 K and irradiated with X-rays using a 5-BKhV-6(W) tube with a tungsten anode (33 kV, 80 mA) during 90 min through an aluminum foil window. The IR spectra were recorded with a PerkinElmer 1720X FTIR spectrometer (MCT detector, 1 cm^{-1}, 200 scans) at 7.5 K. The EPR spectra were measured in a temperature range of 7–50 K using an X-band (9.4 GHz) EPR spectrometer with a 100 kHz magnetic field modulation (SPIN, St. Petersburg).

an extremely broad (virtually invisible) EPR signal in disordered media.[13] In agreement with this mechanism, the signal assigned to the diacetyl radical anion is not observed in the presence of Freon 11, and the EPR spectrum of the irradiated Freon 11/diacetyl/dimethyl ether mixture (1:2:200) shows only a broad triplet of $^{\bullet}CH_2OMe$.

The IR spectrum of the deposited diacetyl/dimethyl ether mixture reveals a relatively intense absorption band at 1715 cm^{-1} [Figure 1(*b*)] due to the C=O stretching of the diacetyl molecule[14,15] (no such a band can be seen in the IR spectrum of pure deposited dimethyl ether). Other absorption bands of diacetyl are much weaker and overlap with the strong absorption bands of the dimethyl ether matrix; thus, they cannot be observed in our experiment. The irradiation leads to a decrease in the absorption at 1715 cm^{-1} (by about 5%) and the appearance of a new absorption band at 1396 cm^{-1}, which is not found in the irradiated neat dimethyl ether. This band does not show any changes in intensity upon annealing, at least, up to 50 K. For the mixture containing Freon 11, the intensity of absorption at 1715 cm^{-1} does not change after the irradiation and no band at 1396 cm^{-1} appears. Thus, the behavior of the band at 1396 cm^{-1} correlates well with that of the EPR signal of diacetyl radical anions. Note that it is the only measurable new radiation-induced absorption observed in the diacetyl/dimethyl ether sample and not in the neat dimethyl ether (within the available spectral window in this matrix).

To make an unequivocal assignment, we have carried out a series of quantum-chemical calculations on diacetyl and its radical anion at the MP2 and CCSD levels (as implemented in our code[16]) with the correlation-consistent basis sets[17] of increasing size augmented with diffuse functions. The computed harmonic vibrational frequencies and their relative IR intensities for the neutral diacetyl molecule match well the known experimental data.[14,15] In particular, the computed frequency of the most intense C=O asymmetric stretching band (1738 cm^{-1}, intensity of 168 km mol^{-1}) is in agreement with that measured in the dimethyl ether matrix. The computations reveal only the *trans* conformer of the neutral molecule, and a *cis* transition state 6 kcal mol^{-1} higher. The radical anion has two minima separated by a barrier of ~33 kcal mol^{-1}, the *trans* isomer being ~8 kcal mol^{-1} lower in energy. The adiabatic electron affinity of diacetyl (~0.5 eV at both MP2 and CCSD levels of theory) is comparable to the known value of 0.69±0.10 eV.[18] The strongest vibration band (of C=O asymmetric stretching character) of the C_{2h} symmetric *trans* isomer is predicted at 1438 cm^{-1}, in reasonably good agreement with the observed band at 1396 cm^{-1}, taking into account the effects of anharmonicity, intermolecular interactions and the imperfections of the computational method. Note that the computed intensity of this band for the radical anion (422 km mol^{-1}) is much higher than that for the neutral molecule, explaining the observation of this species, despite the rather low conversion of diacetyl molecules in the dimethyl ether matrix. Other IR active vibration bands computed for the *trans*-diacetyl radical anion are markedly weaker and overlap with the absorptions of dimethyl ether, being unobserved in our experiment. For the C_2-symmetric *cis* isomer, the computations predict two strong vibration bands (at 1645 and 1517 cm^{-1}), not seen in the experiment. All computed values can be found in Online Supplementary Materials.

Thus, both our experiments and computations confirm the assignment of absorption at 1396 cm^{-1} to the asymmetric C=O stretching in the *trans*-diacetyl radical anion and demonstrate the extremely large red shift of this vibration (by more than 300 cm^{-1}). Such a shift reflects the dramatic weakening of the carbonyl C=O bonds upon electron attachment, their lengths increasing by 0.054 Å (from 1.217 to 1.271 Å), the bond order changes from 2 to ~ 1.5. At the same time, the central C–C bond becomes shorter by 0.097 Å (from 1.538 to 1.441 Å), the bond order going from 1 to ~1.5.

In summary, we have obtained the first direct IR-spectroscopic evidence for the strongest vibrational feature of the diacetyl radical anion in a low-temperature molecular matrix supported with the EPR data, the chemical arguments (effect of electron scavenger) and the high-level quantum-chemical calculations. The methodology applied in this work can be used for the vibrational spectroscopic characterization and the interpretation of chemical bonding in unstable radical anions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.07.011.

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