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Effect of Matrix Electronic Characteristics on Trapping and Degradation of Organic Radical Cations in Solid Rare Gases: A Case Study of Methylal Radical Cation[†]

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The matrix effects on trapping and degradation of methylal radical cation generated in solid argon, krypton, and xenon doped with an electron scavenger at 16 K were investigated by EPR spectroscopy. A relatively weak characteristic signal from trapped methylal radical cations was recorded in an argon matrix. However, the most intense signals in this matrix result from the products of degradation of the primary cations, mainly methyl and methoxy radicals. A comparatively low $g_{\max}$ value for methoxy radical ($g = 2.032$) was explained by formation of a π-complex [$CH_3O^\bullet ...CH_2{=}O^+CH_3$] upon fragmentation of the parent cation in solid argon. In the case of a xenon matrix, the main observed species is the $CH_3O^\bullet CHOCH_3$ radical, which appears to result from proton loss in the primary cation. Both deprotonation and fragmentation products were found in krypton. The matrix effects were attributed to the variations in ionization potentials and polarizability (or basicity) of matrix atoms. Fragmentation predominating in argon was explained by excess energy resulting from highly exothermic positive hole transfer. Deprotonation in xenon is favored by basicity of the matrix atoms. Two possible mechanisms were discussed for the latter case, i.e., thermodynamic effect (deprotonation to matrix) and kinetic effect (catalysis of intramolecular H shift by matrix atoms).

1. Introduction

Reactive organic radical cations resulting from ionization of parent neutral molecules are fundamentally important species, which occur in a wide variety of physical and chemical processes ranging from interstellar chemistry to catalysis. Since the 1960s matrix isolation combined with optical absorption spectroscopy has been extensively applied to characterization of radical cations, especially of aromatic and other conjugated systems.[1a−d] Nevertheless, the structure and properties of a large number of chemically important aliphatic radical cations were actually unknown before 1980. The progress in this field is associated largely with the so-called "Freon technique" introduced by Shida and Kato.[2] This rather simple method implies generation of solute cations by irradiation of frozen glassy or polycrystalline solutions of organic molecules in halocarbon (mainly Freon) matrixes characterized by high ionization potentials (IP) and electron affinity. Unlike earlier approaches, the "Freon technique" uses essentially EPR spectroscopy as a probing tool, which made it possible to get detailed information on the electronic structure and geometry of organic radical cations.[3a,b] The most important limitations of this method are concerned with relatively strong cation−matrix interactions and the unknown structure of the frozen Freonic solutions. In fact, the matrix effects on the structure and reactivity of trapped cations in Freons can be hardly rationalized in simple, clear physical terms. The complications may be especially significant for highly reactive radical cations and for species with nearly degenerate electronic states.

An alternative method for EPR studies of radical cations involves ionization of organic molecules adsorbed in porous media, like silica gel[4a] or synthetic zeolites.[4b,c] Although this approach was tested mainly for hydrocarbon cations, the significance of specific physical and chemical matrix effects for the radical cations trapped in porous media is beyond any doubts.[5] Moreover, at present it is not clear whether heteroatomic radical cations (e.g., ethers, esters, amides, etc.) can be stabilized in zeolites and related matrixes.

After all, using a rigorous ("classic") matrix isolation approach appears to be the most direct way to obtain basic information on the structure and properties of radical cations in a low-disturbing environment. Meanwhile, up to recently only a few simple organic cations were characterized by EPR in solid rare gas matrixes. In particular, Knight et al. reported detailed analysis of the EPR spectra of several small radical cations in neon matrixes.[6a−c] Although solid neon seems to be a nearly perfect medium for basic spectroscopic studies of small species, this may not be the best choice for larger cations of chemical interest. On the other hand, Qin and Trifunac used a xenon matrix doped with an electron scavenger in order to isolate the relatively large radical cation produced from 1,1,2,2-tetramethylcyclopropane.[7] To the best of our knowledge, it was the only EPR study of organic radical cation in a rare gas matrix other than neon reported before 1996. It is worthwhile noting that the EPR spectra of radical cations under consideration were not recorded in solid argon, which is the most common medium for matrix isolation spectroscopy.

Since 1995 we started extensive studies aiming at characterization of various types of organic radical cations and products of their transformations in solid rare gas matrixes by a combination of EPR and IR spectroscopy.[8−12] The cations were generated by fast electron irradiation of solid-deposited argon, krypton, or xenon doped with studied compounds and electron

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scavengers.[13] It was shown[10,12,14] that addition of the scavenger was actually significant when using these matrixes (in contrast with Knight's finding for a neon matrix[6a,c]). Strong enhancement of the cation yield in the presence of charge balancing "electron traps" (scavengers) is quite common for matrix isolation studies.[1a−c] The role of scavengers can be easily understood by taking into consideration the following formal scheme of the formation of paramagnetic species, e.g., for xenon (RH is an organic molecule):

$$\mathrm{Xe} \rightarrow \mathrm{Xe}^{\bullet+} + \mathrm{e}^- \qquad (1)$$

$$\mathrm{Xe}^{\bullet+} + \mathrm{RH} \rightarrow \mathrm{RH}^{\bullet+} + \mathrm{Xe} \qquad (2)$$

$$\mathrm{RH}^{\bullet+} + \mathrm{e}^- \rightarrow \mathrm{RH}^* \qquad (3)$$

$$\mathrm{RH}^* \rightarrow \mathrm{R}^\bullet + \mathrm{H}^\bullet \qquad (4)$$

Addition of a scavenger S leads to ceasing of ion−electron recombination (3) due to efficient electron capturing:

$$\mathrm{S} + \mathrm{e}^- \rightarrow \mathrm{S}^{\bullet-} \qquad (5)$$

As a result, the yield of neutral species produced in reaction 4 should decrease, whereas the probability of cation trapping increases remarkably. In complete accordance with this scheme, we revealed a drastic decrease in the yield of hydrogen atoms from heptane in the presence of a Freon electron scavenger; simultaneously, the signal from alkyl radicals observed without Freon is almost completely replaced by the signal from heptane radical cations.[10,14] Using a similar approach, we obtained the EPR spectra of several medium-size organic radical cations in an argon matrix.[11,12,15] In all cases, addition of a scavenger resulted in a sharp decrease in the yields of trapped hydrogen atoms (at least, by an order of magnitude), which appears to be a clear indication of the efficiency of electron scavenging. However, the relative yields of the trapped radical cations varied dramatically for various systems. In some cases (heptane in xenon,[9,10] benzene and toluene in argon[11,15]), the signals from primary radical cations strongly predominated in the EPR spectra, whereas in other cases (pentane in xenon,[10] dimethyl ether and methylal in argon[12]) the spectra revealed large (or even predominating) contributions from various-type neutral radicals. Furthermore, we failed to observe the EPR spectra of radical cations in a number of systems (C5−C7 alkanes in argon,[9] simple ethers in xenon[12]). The striking difference in the behavior of systems under discussion is unlikely due to solute molecule aggregation and/or inefficient energy transfer. Indeed, if it were the case, one should expect considerably lower yields of the products resulting from solute. However, the total yields of paramagnetic species produced from solute and the total yields of consumption of parent molecules as estimated from IR spectroscopic data[8,12] do not show large variations. As mentioned above, the efficiency of electron scavenging evidenced by suppression of hydrogen atom formation is high in all the systems. Thus, the most reasonable explanation is that the primary radical cations undergo some kind of secondary reaction, which is rapid enough to compete with the trapping process:

$$\mathrm{RH}^{\bullet+} \rightarrow \text{products} \qquad (6)$$

One of the most interesting findings is matrix dependence of the reactions of type (6). The composition of radical products observed in argon and xenon was found to be essentially different in most cases; moreover, some radical cations exhibited nearly complete "switching" between the reaction channels when turning from xenon to argon.[12] The matrix effects observed in the chemically simplest, atomic media should be of some basic physical origin because of the absence of complications resulting from specific interactions, complex formation, etc., which commonly occur in molecular matrixes. To explain the results, we suggested that the difference was due to variations in electronic properties, i.e., the IP and polarizability of the matrix atoms. Detailed information on the effects of this kind could be of basic interest for matrix isolation and chemistry of the radical cations in condensed phases.

The aim of the present work is to study the matrix effect on trapping and degradation of a specific radical cation in various solid rare gases. Methylal (dimethoxymethane) appears to be a very suitable model for the investigation of this kind. Indeed, methylal radical cation exhibits a $p-\sigma-p$ SOMO delocalized over the $-\mathrm{O}-\mathrm{CH}_2-\mathrm{O}-$ fragment, which manifests itself in the appearance of characteristic, extremely large hyperfine coupling with the protons of the CH_2- group.[16] In the frame of semiquantitative quantum chemical consideration, such a structure may imply certain weakening of both C−O and C−H bonds upon ionization of the parent methylal molecule.[17] For this reason, the radical cation has two potential reaction channels, i.e., C−H bond cleavage (deprotonation) and C−O bond cleavage (fragmentation). Evidence for both kinds of reactions was obtained in Freon matrixes.[18] A preliminary indication of matrix-controlled "switching" between the reaction channels for methylal radical cation in argon and xenon was obtained in our recent studies.[12] In the present paper, we report detailed analysis of the products resulting from methylal radical cation in various solid rare gas matrixes.

2. Experimental Section

The experimental procedure was described in detail previously.[9−12] High-purity rare gases (>99.99%) were used. Specifically deuterated methylal-d_6 ($\mathrm{CD_3OCH_2OCD_3}$) was synthesized from paraform and methanol $\mathrm{CD_3OH}$.[19] Freon-11 ($\mathrm{CFCl_3}$) used as an electron scavenger was purified by passing through the column packed with $\mathrm{Al_2O_3}$. An original continuous-flow helium cryostat for EPR studies with vacuum resonator cavity[9,10] was used.

The samples were obtained by slow controlled deposition (typically, 1−2 h) of the gaseous mixtures containing 0.1−0.2 mol % of methylal and 0.2−0.4 mol % of Freon-11 onto the tip of cooled sapphire rod inserted into the resonator cavity. The deposition temperature was typically 45 K for xenon, 30−32 K for krypton, and 18−20 K for argon. After the deposition was complete, the samples were irradiated with fast electrons (1.2 MeV) at 15−16 K using a EG-2.5 Van de Graaff type accelerator up to the dose of 20 kGy. The EPR spectra were measured at 9−60 K using an X-band (9.3 GHz) spectrometer with a 100 kHz magnetic field modulation manufactured by SPIN (St. Petersburg, Russia). Unless otherwise stated, low microwave power (ca. 0.005 mW) was used to avoid signal saturation. In some experiments, the EPR signals were tested for photobleaching with visible light using a 100 W tungsten lamp with aqueous heat shield (the sample temperature did not rise during photolysis, as proved by continuous monitoring).

3. Results

3.1. Methylal in a Xenon Matrix. EPR spectrum of the irradiated deposited xenon matrix containing methylal and Freon-11 is shown in Figure 1. The central part of the spectrum exhibits a characteristic anisotropic poorly resolved doublet

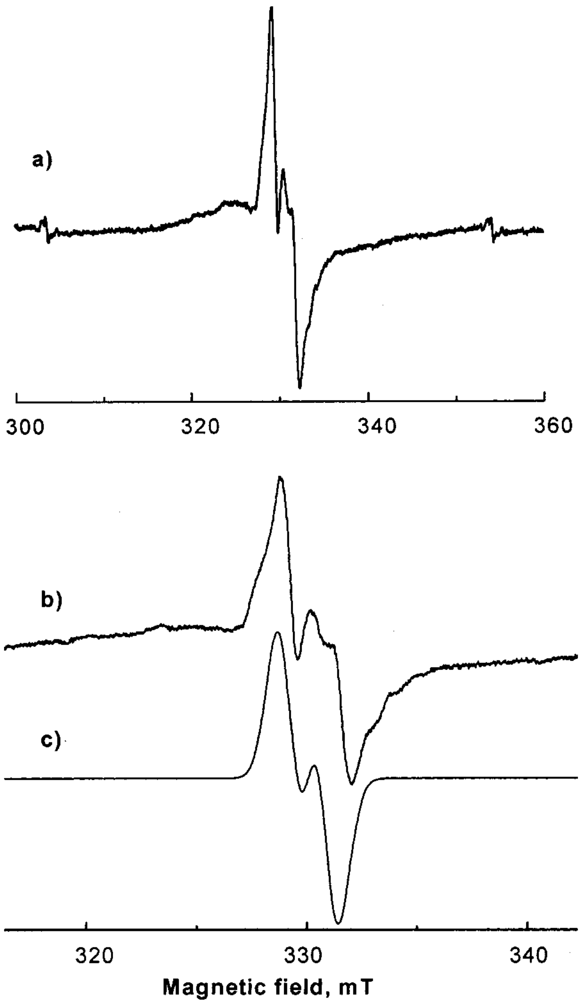

Figure 1. (a, b) EPR spectra of deposited mixture methylal/xenon/Freon-11 (mole ratio 1/500/2) irradiated with fast electrons and measured at 16 K. (c) Powder simulated spectrum of the $CH_3O^{\bullet}CHOCH_3$ radical (see text for details).

signal, which is typical for $-O^{\bullet}CHO-$ type radicals. A very similar spectrum was observed for the radicals resulting from irradiation of polymethylene oxide at 77 K.[20] In the case of methylal, such a signal should be naturally assigned to the $CH_3O^{\bullet}CHOCH_3$ radical. As shown in Figure 1c, the spectrum can be reasonably simulated using an α-proton hyperfine coupling tensor with the principal components of $A_{XX} = 2.4$ mT (67 MHz), $A_{YY} = 0.3$ mT (8.4 MHz), and $A_{ZZ} = 1.2$ mT (33.6 MHz) (as usual, it is assumed that the *X*-axis is perpendicular to the C−H bond in the radical plane, the *Y*-axis coincides with the C−H bond direction, and the *Z*-axis is normal to the radical plane).[21] These parameters are close to the corresponding values reported for the $-O^{\bullet}CHO-$ type radical in polymethylene oxide.[20]

Warming the sample to 30−60 K results in reversible narrowing of the doublet lines and certain decay of the signal. No indication of the chemical transformation of the observed radical was found under the experimental conditions used.

The signal from $CH_3O^{\bullet}CHOCH_3$ radicals strongly predominates in the EPR spectrum recorded in a xenon matrix. The central region of the spectrum may also contain a minor contribution from other radicals, which result in some distortion in the signal shape. In addition, the spectral wings reveal the presence of a very weak signal from hydrogen atoms (a characteristic doublet with the splitting of ca. 50.6 mT and superhyperfine structure due to interaction with magnetic nuclei of the xenon matrix). However, the relative concentration of trapped hydrogen atoms is extremely small (less than 2% of the total amount of paramagnetic species). It is worthwhile noting that an intense signal from H atoms is clearly observed in the sample containing only methylal in a xenon matrix, without electron scavenger; in the latter case, the concentration of trapped hydrogen atoms is comparable to those of neutral radicals from methylal. This implies that hydrogen atoms do not react with methylal molecules in a xenon matrix under experimental conditions used, and the suppression of H atom yield in the presence of Freon is clearly due to the effect of electron scavenger on precursor formation, in accordance with the reaction scheme (1)−(5). Thus, the electron scavenging appears to be quite effective, and the $CH_3O^{\bullet}CHOCH_3$ radicals observed in a xenon matrix in the presence of Freon additive should result from the reactions of the primary methylal radical cations, which are not trapped under the conditions of our experiment.

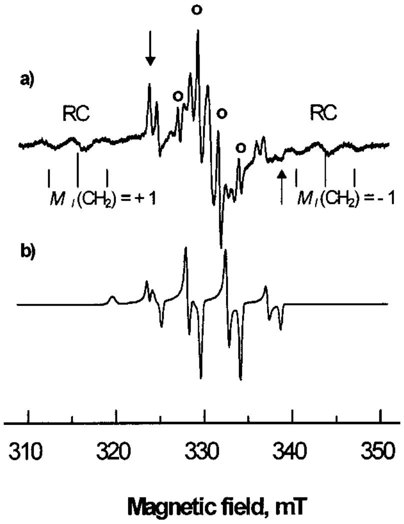

Figure 2. (a) EPR spectrum of deposited mixture methylal/argon/Freon-11 (1/500/2) irradiated with fast electrons and measured at 16 K. (b) Powder simulated spectrum of methoxy radicals (see text for details). The stick diagram shows the assignment of our triplets to the methylal radical cation. Arrows indicate the positions of the lines assigned to the signals of alkoxy radicals (g_2 and g_3 components; see text for details). The lines from the methyl radical are marked with circles.

We failed to detect any measurable amounts of the trapped methylal radical cations in a xenon matrix in the presence of an electron scavenger. As will be illustrated below, these species could be easily observed, even if they occur in small concentrations.

3.2. Methylal and Methylal-d_6 in an Argon Matrix. In the case of methylal in argon, addition of the Freon additive again results in drastic suppression of hydrogen atom formation, so the criterion of effective electron scavenging discussed above is fulfilled. The EPR spectrum of an irradiated solid mixture argon/methylal/Freon-11 is shown in Figure 2. One can see that the spectral pattern is rather complicated and completely different from that observed in a xenon matrix. First, the spectrum shown in Figure 2 reveals a clear indication of trapping of the primary methylal radical cations. The spectrum of these species is basically a triplet of triplets;[16] the major triplet splitting [a(2H) = 14 mT] results from hyperfine coupling with the methylene group protons, whereas a smaller splitting of a(2H) = 3.4 mT is due to two of six methyl protons (one from each CH_3 group). Because of the extremely large coupling constant for methylene protons, the outer triplets corresponding to

$M_I(CH_2) = \pm1$ do not overlap with the signals from any other radicals present in the system. As shown in Figure 2, these features are quite characteristic and clearly distinctive at the spectral wings, despite their low intensity. The central triplet corresponding to $M_I(CH_2) = 0$ is essentially "hidden" because of strong overlapping with other signals. The observed hyperfine coupling parameters are rather close to those reported in a Freon matrix.[16] We should note that the methyl groups in the methylal radical cation are rigidly fixed, so only two of six methyl protons yield significant hyperfine coupling in both Freon and argon matrixes.

Meanwhile, as revealed by double integration (taking into account intensity ratio), the observed signals from methylal radical cations account for roughly 10% of paramagnetic species trapped in argon in the presence of electron scavengers. Thus, a major part of the primary cations appears to yield secondary radicals in some rapid processes, which compete with trapping. A relatively sharp well-defined quartet signal with a characteristic splitting of 2.30 mT (marked with circles) should be definitely assigned to methyl radicals.[22] Analysis of the experimental spectrum also provides some evidence for the formation of radicals of $ROCH_2^\bullet$ type, which yield an anisotropic triplet signal with an observed line separation of ca. 1.9 mT. The component corresponding to $M_I = 0$ clearly appears as a central line of the spectrum, whereas the components with $M_I = \pm1$ probably overlap with other species.

In addition to the signals discussed above, the spectrum shown in Figure 2, reveals rather intense anisotopic features (marked with arrows), which cannot be ascribed to any carbon-centered radical. Indeed, the positions of these lines imply unusually large coupling constants, and the signal shape exhibits noticeable anisotropy of the *g*-factor. The most reasonable explanation of the origin of these features is concerned with formation of the oxygen-centered alkoxy-type radicals. In line with this interpretation, the components under consideration, unlike the lines from other species, show no appreciable signal saturation at high microwave power (up to 5 mW). Such a behavior is a characteristic of the radicals with large spin−orbit coupling. Note that the signals from alkoxy-type radicals should also exhibit additional lines between the features marked with arrows, which overlap with other signals.

The signal from $CH_3O^\bullet CHOCH_3$ radicals predominating in a xenon matrix cannot be identified unambiguously in the case of argon. This doublet may overlap partially with the lines from other species, in particular, with the components corresponding to $M_I = \pm{}^1/_2$ of methyl radicals. In any case, the contribution of $CH_3O^\bullet CHOCH_3$ radicals to the spectrum observed in argon should be relatively small, and the formation of these species is not the main path of reactions of the primary methylal radical cations in an argon matrix.

Warming the sample above 20 K results in a gradual decrease in the intensity of lines from methyl radicals, whereas other radical species observed in argon are stable, at least up to 32 K.

EPR spectrum of irradiated system argon/methylal-d_6/Freon-11 is shown in Figure 3. Using a specifically deuterated molecule allowed us to give more definite identification and provided some important mechanistic clues. The substitution of H for D atoms results in a decrease of the corresponding hyperfine coupling constants by the factor of $\mu_H/\mu_D = 6.51$. As expected, the splitting of the outer components $M_I(CH_2) = \pm1$ of the signal from methylal radical cation is not observed, because the coupling constants with deuterons of the CD_3 groups are too small to be resolved. As reported previously,[18] the spectrum of the methylal-d_6 cation in a $CFCl_3$ matrix is a broadened 1:2:1 triplet with a hyperfine splitting of 13.6 mT due to methylene protons. This value is very close to the splitting constant of 14.0 mT estimated as one-half of the separation between the outer components observed in argon (central component of the triplet is hidden by the lines of neutral radicals). We should note that the components assigned to the radical cation almost disappear after photolysis with visible light (30 min), whereas the lines from neutral species are essentially unaffected.

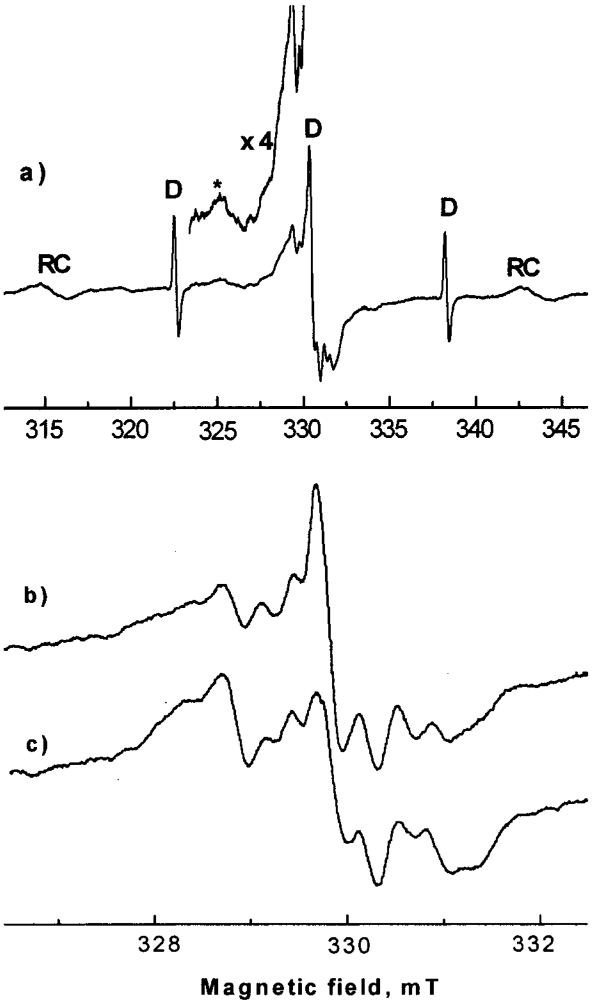

Figure 3. (a) EPR spectrum of deposited mixture methylal-d_6/argon/Freon-11 (1/500/2) irradiated with fast electrons at 16 K. The asterisk shows the feature assigned to the g_{max} component of the $CD_3O^\bullet$ radical. The outer components of the signal from the methylal-d_6 radical cation ($M_I = \pm1$) are marked with RC. The positions of lines from trapped D atoms are also shown. (b) and (c) show the central region of the spectrum for the same system obtained immediately after irradiation and after annealing the irradiated sample at 32 K, respectively. All the spectra were measured at 16 K.

Extended hyperfine structure observed in the central region in the case of protiated methylal is collapsed due to small coupling constants in deuterated radicals. In particular, $CD_3^\bullet$ radicals, observed instead of $CH_3^\bullet$, yield a septet spectrum (nuclear spin of D is 1) with the hyperfine splitting of 0.35 mT. Similarly, $CD_3OCH_2OCD_2^\bullet$ radicals should give a quintet spectrum with the splitting of ca. 0.29 mT. Indeed, the central part of the spectrum given in Figure 3 shows a complicated pattern with the characteristic splitting of 0.3−0.35 mT, which may be a superposition of the signals from different deuterated radicals (narrow component corresponding to $M_I = 0$ of the

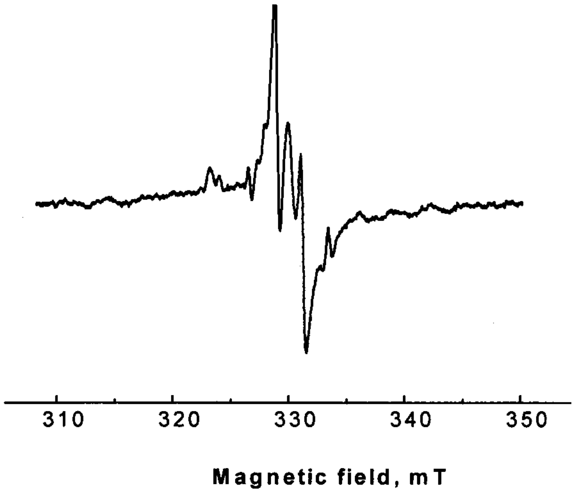

Figure 4. EPR spectrum of deposited mixture methylal/krypton/Freon-11 (1/500/2) irradiated with fast electrons and measured at 16 K.

signal from trapped D atoms also contributes to the central line). The only indication of proton coupling can be found for a doublet-type broad signal, which can be attributed to the $CH_3O^\bullet CHOCH_3$ radical. The contribution of this species increases upon annealing the sample simultaneously with decay of $CD_3^\bullet$ radicals and D atoms (Figure 3c,d), which may indicate a hydrogen abstraction reaction. On the other hand, the triplet signal with the splitting of ca. 1.9 mT is not detected in the case of methylal-d_6, which argues against formation of the $CD_3OCH_2^\bullet$ radicals.

A noticeable feature of the spectra shown in Figure 3 is the absence of signals tentatively assigned to alkoxy-type radicals in the case of protiated methylal. Instead of these, a relatively weak and broad feature marked with an asterisk in Figure 3 appears at the low-field side, in the region of $g \approx 2.03$. This result implies that the specific deuteration directly affects the radical site; i.e., the alkoxy-type species responsible for the signals observed in an argon matrix should be $CD_3O^\bullet$ (respectively, $CH_3O^\bullet$ in protiated methylal) rather than $CD_3OCH_2O^\bullet$ ($CH_3OCH_2O^\bullet$ for protiated molecule). In this case, the low-field feature should correspond to the g_{max} component of the anisotropic powder spectrum. We reserve further detailed consideration for the Discussion.

3.3. Methylal in a Krypton Matrix. Figure 4 shows the EPR spectrum recorded after irradiation of methylal in a krypton matrix in the presence of Freon-11. One can see that this spectrum is actually a superposition of signals observed in xenon and argon. Indeed, the doublet signal from the $CH_3O^\bullet CHOCH_3$ radical identified as the main paramagnetic species in xenon is quite distinguishable and rather intense in a krypton matrix too (Figure 4). On the other hand, the spectrum actually reveals the signals of all the species identified in an argon matrix (although the corresponding signals observed in the case of krypton are relatively weaker). The trapped methylal radical cation again manifests itself in weak features at the spectral wings. The quartet signal of methyl radicals is easily recognized due to the components corresponding to $M_I = \pm ^3/_2$, which do not overlap with other lines. Also, it is possible to reveal the features, which were tentatively attributed to the alkoxy-type radicals in the case of argon, and the central line probably arising from the $ROCH_2^\bullet$ type radical (see above). Thus, the degradation of the primary methylal cations in a krypton matrix occurs via both the "xenon mode" and "argon mode". We should note that the yield of trapped radical cations in krypton is also small.

Warming the sample to 30−50 K leads to a decay of methyl radicals. Other species were found to be more stable in a krypton matrix.

4. Discussion

4.1. Identification of Methoxy Radicals. The identification of carbon-centered radical species in the system under consideration appears to be quite straightforward. Meanwhile, the assignment of the alkoxy-type radical deserves special consideration. The specific features of the structure of π-electronic oxygen-centered species of this kind are concerned with orbital degeneracy, which implies easy promotion of an electron from the lone-pair orbital to the singly occupied orbital of the oxygen atom. In the solid phase this formal degeneracy is actually lifted because of matrix interaction. Nevertheless, the separation between the two orbitals is still small, which results in a large positive shift of the g_{max} value in alkoxy radicals.[23,24] Furthermore, because of the very large anisotropy of the g-factor, the alkoxy-type radicals yield very broad and weak spectra in disordered media, so the observation of the corresponding signals becomes problematic, especially in low-interacting inert media. Thus, recording of rather intense, distinct features of alkoxy-type radicals in solid argon is somewhat surprising and requires specific justification.

First, we need to recall the arguments in favor of spectral assignment. The carbon-centered radicals, which can be produced from the methylal molecule ($CH_3^\bullet$, $CH_3O^\bullet CHOCH_3$, and $ROCH_2^\bullet$), give the signals with a nearly isotropic g-factor centered around $g \approx 2.00$. Of all these species, methyl radicals yield the spectrum with the largest total spread of ca. 7 mT (±3.5 mT of the signal center). Meanwhile, the features marked with arrows in Figure 2 are separated by ca. 14−15 mT, which is qualitatively consistent with the sum of coupling constants for β-protons in alkoxy-type radicals.[23,24] In addition, the observed line shape indicates marked g anisotropy, and the saturation behavior gives some evidence for spin−orbit coupling. In principle, there are two possible structures of the alkoxy-type radicals in the system under consideration, namely $CH_3O^\bullet$ and $CH_3OCH_2O^\bullet$; however, the experiments with specifically deuterated methylal allow us to make a choice in favor of $CH_3O^\bullet$. It is worthwhile noting that the formation of the methoxy radical from the methylal cation looks quite logical from a mechanistic point of view. Indeed, the fragmentation process

$$CH_3OCH_2OCH_3^{\bullet +} \rightarrow CH_3O^\bullet + CH_3O^+{=}CH_2 \qquad (7)$$

occurs with rather high yield under the conditions of the mass-spectrometric experiment.[25,26] The formation of large amounts of methoxy radicals in the liquid-phase radiolysis of methylal was also proved by the spin trapping technique.[27]

However, despite this reasoning, the assignment of the observed spectral features to methoxy radicals is not solid, because direct proof of a large positive g shift is lacking. To establish this shift, it is important to observe the outermost low-field component of the signal corresponding to $g = g_{max}$ and $M_I = +^3/_2$. This line may be weak and broad or overlap with the components from the methylal radical cation in the the case of protiated methylal. However, for $CD_3O^\bullet$ radicals from methylal-d_6 the hyperfine coupling becomes much smaller, and the signals resulting from the g_{max} (g_1) component for different M_I values should be "integrated" in one broad low-field feature with poorly defined structure. We believe it is this feature that is marked with an arrow in Figure 3. In this case, we can estimate $g_1 \approx 2.032$. At first glance, such a value seems to be unusually small for an alkoxy-type radical. Indeed, $CH_3O^\bullet$ in crystalline methanol at 4.2 K exhibits $g_{max} = 2.088$;[24] rather close values (2.054−2.093) were obtained for other alkoxy radicals.[23] However, Symons and Wren[28] reported $g_{max} = 2.028$ for the alkoxy-type radical resulting from the *s*-trioxane radical cation. It should be noted that the g_{max} value depends crucially on the interaction of an oxygen-centered radical with the environment. The stronger interaction results in a larger separation between the singly occupied orbital and lone-pair orbital and, therefore, in a smaller g shift (i.e., lower g_{max} value). In most cases (like in crystalline methanol[24] or nucleosides[23]), it is assumed that the interaction is dominated by hydrogen bonding. Symons and Wren[28] suggested reasonably that the interaction may be even stronger in the case of formation of a π-complex between alkoxy radical and $RO^+{=}CH_2$ type cation resulting from C−O bond cleavage in trioxane radical cation. Actually, this situation is quite similar to that occurring for the methoxy radical produced from the methylal radical cation: fragmentation (7) in a rigid argon matrix naturally results in formation of the π-type complex of a $CH_3O^\bullet$ ($CD_3O^\bullet$) radical with methoxymethyl cation, which can be depicted as $[CH_3O^\bullet ... CH_2{=}O^+CH_3]$ or $[CH_3O^\bullet ... {}^+CH_2OCH_3]$ in view of "charge-resonance" structures. The formation of such a complex may explain the effective removal of orbital degeneracy in $CH_3O^\bullet$ in a seemingly inert matrix environment, which leads to a relatively low g_{max} value and appearance of distinct features of the radical in the powder EPR spectrum.

Now we may turn back to the protiated methylal. As the symmetry of the g-tensor for alkoxy radicals is not truly axial,[23,28] the splitting of both low-field and high-field features marked with arrows may be assigned basically to relatively close g_2 and g_3 components of the signals corresponding to $M_I = +^3/_2$ and $M_I = -^3/_2$, respectively. The coupling with β-protons in alkoxy-type radicals is virtually isotropic; the hyperfine coupling constant may be estimated roughly as one-third of the distance between outer components. To obtain more accurate estimates, we performed a series of simulations. The spectrum shown in Figure 2c was simulated using the following parameters: $g_1 = 2.032$, $g_2 = 1.998$, $g_3 = 2.007$, $a_{\beta-H}(3H) = 4.5$ mT. The values of g_2, g_3, and $a_{\beta-H}$ are in reasonable agreement with those reported for alkoxy radicals previously.[23,24] One can see that the outermost, relatively weak low-field component ($g = g_1$, $M_I = +^3/_2$) actually falls in the region occupied by the signal from methylal radical cation, and the inner lines of methoxy radical ($M_I = \pm^1/_2$) overlap with the signals from other paramagnetic species. Note that the agreement with the experimental spectrum is qualitative, and the signal shape is not fully reproduced; one possible reason is concerned with radical dynamics, which was not taken into account.[29] Nevertheless, we believe that the basic assignment is correct.

In the case of $CD_3O^\bullet$, the hyperfine coupling constant should be scaled by the factor of 6.51, which yields $a_{\beta-D}(3D) = 0.69$ mT, i.e., roughly twice as large as the coupling constants with D atoms in the carbon-centered radicals discussed above. For this reason, the components of the hyperfine structure of deuterated methoxy radicals should strongly overlap with the lines from other species observed in the central region of the spectrum shown in Figure 3.

4.2. Effect of Matrix Electronic Characteristics on the Reactions of Primary Methylal Radical Cations. The most interesting result obtained in this study is concerned with the nearly complete difference in the composition of radical products resulting from methylal cations in argon and xenon. The indications of this effect referred to as "matrix switching" between reaction channels[12] was also obtained for some other systems; however, the case of methylal appears to be the most illustrative. As a whole, the products of C−H bond rupture (actually, deprotonation) predominate in xenon, whereas the products of C−O skeleton bond rupture are the most abundant species in argon (krypton exhibits a sort of compromise).

As was briefly discussed previously,[12] the probability of trapping of the primary radical cations and mechanism of their degradation should be controlled by some basic physical properties of matrix atoms. First, one should consider matrix IP, which determines the so-called "IP gap" between the matrix atom and solute molecule. The significance of this characteristic was stressed in a number of studies; however, its actual role for different systems is not so clear. On the basis of experiments with small molecules in neon and argon, Knight[6a] concluded that trapping of isolated radical cations required a sufficiently large "IP gap" (5 eV or higher). However, this criterion appears to be not applicable directly to larger organic molecules, especially, in more interacting media. Indeed, the formation of, at least, two hydrocarbon cations (1,1,2,2-tetramethylcyclopropane[7] and *n*-heptane[9,10]) in xenon is well documented, in spite of the rather small "IP gap", as estimated from gas-phase values (ca. 2−2.5 eV). It is also worthwhile noting that various-type organic radical cations are readily produced in high yields by positive hole transfer in Freon matrixes, where the gap values are as low as 1.5−2 eV. Thus, the absence of trapped methylal radical cations in a xenon matrix is unlikely due to a small "IP gap". It is necessary to consider other reasons, which will be done later.

On the other hand, large gap values (>4−5 eV) result in high exothermicity of positive hole transfer, which means rather high excess energy obtained by solute radical cations. For complex molecules, this excess energy may exceed the bond dissociation energy in the resulting cation, so rapid fragmentation or rearrangement following hole transfer becomes highly probable. This is particularly true for aliphatic cations in argon because of inefficient dissipation of excess energy to the matrix lattice due to the absence of appropriate matrix phonon modes. An indication of fragmentation of the primary cations produced from propane and isobutane in argon was reported by Gotoh et al.[30] Some rearrangements induced by the excess energy effect under discussion were revealed in optical spectroscopic studies of more complex systems in argon.[1c,31] Detailed investigations of the products resulting from C5−C7 linear alkanes in argon by EPR and IR spectroscopy made in our laboratory provided clear evidence for efficient fragmentation of the primary radical cations.[8,10] The predominant mode of fragmentation was found to be C(1)−C(2) bond rupture. We believe reasonably that the similar-type excess energy effect is responsible for the observed skeleton fragmentation of methylal radical cations in argon. In addition to reaction 7 discussed above, the fragmentation also yields methyl radicals:

$$CH_3OCH_2OCH_3^{\bullet +} \rightarrow CH_3^{\bullet} + CH_3OCH_2O^+ \qquad (8)$$

Both processes (7) and (8) occur in krypton, however, with relatively smaller yields. Meanwhile, we have no evidence for such reactions in xenon, which is quite in line with the explanation based on "IP gap" consideration implying that the excess energy obtained by the cation in xenon is too small. It should be noted that the fragmentation under consideration probably occurs from vibrationally excited states, in competition with trapping, whereas the relaxed methylal radical cations trapped with small yields in argon and krypton are thermally stable in both matrixes within the temperature range studied. In general, from our experience we may conclude that saturated linear radical cations containing more than three atoms in the main chain can be hardly trapped in argon with reasonably high yields using the radiolysis technique, mostly because of rapid fragmentation induced by excess energy. Meanwhile, aromatic and conjugated radical cations can be easily produced in argon in this way, which was demonstrated in optical absorption studies[1c,32] and in our recent EPR experiments.[11,15] This difference is probably due to the possibility of efficient internal relaxation of excess energy in the latter species; however, more work should be done to clarify this criterion.

Now we can turn back to the nature of processes occurring in xenon. The reaction resulting in formation of $CH_3O^{\bullet}CHOCH_3$ radical from methylal radical cation should be formally characterized as proton loss. Similar-type effects were also observed in our studies of some other radical cations in xenon (e.g., dimethyl ether,[12] tetrahydrofuran and isobutane[33]). In all the cases, the EPR spectra exhibit mainly (or even exclusively) the signals from specific neutral radicals resulting from C−H bond rupture in the parent cation. We should note that deprotonation appears to occur effectively for the radical cations, which are expected to be highly "acidic", if we assume that "acidity" correlates with spin density at specific protons for the corresponding radical cations.[3a] The case of methylal is of special interest because of selectivity of the observed proton loss. Indeed, we found highly preferential abstraction of protons from the central methylene group, which exhibits very high isotropic proton hyperfine coupling constant.[34] This result is in complete accord with the concept of site-selective deprotonation occurring from the maximum spin density position, which was clearly established for linear alkane radical cations[4b,35] and also applied to alkene isomer cations.[36]

The basic conclusion from the above consideration is that the xenon matrix strongly facilitates deprotonation or proton shift processes in the radical cations. In general, it looks rather logical, if one takes into account the high polarizability of xenon atoms, which implies appreciable basicity. Indeed, we can see that the proton affinity of xenon atoms (the highest of all rare gases) is as large as 5.4 eV, that is, close to that of simple carbon-centered organic radicals,[37] which makes deprotonation of some radical cations to xenon only a slightly endothermic process, even in the frame of gas-phase approximation. However, in the solid phase, one should take into account collective proton solvation (i.e., formation of the protonated clusters). IR spectroscopic evidences for formation of the species $Rg_{gn}H^+$ (R_g is a rare gas atom) in argon and krypton was reported by Milligan and Jacox[38] on the basis of re-interpretation of earlier data obtained by Bondybey and Pimental;[39] the formation of similar-type protonated species in xenon was revealed by Karatun et al.[40] More recently, Kunttu et al.[41] presented exhaustive arguments in favor of identification of the protonated species in xenon as linear centrosymmetric cation $XeHXe^+$. This kind of proton stabilization may favor proton transfer to the xenon matrix for highly acidic radical cations. In the case of methylal, this may be formally written as follows:

$$CH_3OCH_2OCH_3^{\bullet +}(Xe) \rightarrow CH_3O^{\bullet}CHOCH_3 + XeHXe^+ \quad (9)$$

To obtain direct proof of reaction 9, it is necessary to observe the formation of both products in the system under consideration by EPR and IR spectroscopy, respectively. The experiments in this direction are in progress now.

The reaction analogous to (9) may also occur, to a certain extent, in the case of krypton; however, it is essentially less probable for argon. In accordance with this consideration, the relative yield of deprotonation product ($CH_3O^{\bullet}CHOCH_3$ radical) strongly increases with increasing the matrix basicity. It is worthwhile noting that, in principle, deprotonation of the most acidic radical cations (e.g., $CH_4^{\bullet +}$) may occur even in argon, but not in neon, which has a much lower polarizability and basicity. Thus, this may be an important factor controlling trapping of small acidic cations, which can explain the failure to obtain some radical cations in an argon matrix (in addition to the "IP gap" criterion mentioned above). To determine the actual role of various factors, it would be of interest to follow the effect of admixture atoms with higher basicity (e.g., argon or krypton) on trapping of the radical cation in solid neon.

The interpretation of the effect of matrix basicity on the properties of solute radical cations in solid rare gases discussed above may be considered a thermodynamic explanation. Meanwhile, a very recent theoretical study of intramolecular H shift in the radical cations in rare gas matrixes[42] provides the basis for an alternative, kinetic explanation of the effect of matrix atoms polarizability and bacisity on trapping of the primary radical cations. The ab initio calculations[42] reveal that the intramolecular H transfer in the methanol radical cation, which exhibits a rather large activation energy in isolated species, can be effectively catalyzed by argon, krypton, or xenon atoms because of lowering the potential barrier due to transition complex formation. In this case, the decrease in barrier height shows a linear correlation with proton affinity of matrix atoms, and xenon acts as the most efficient "catalyst". If it is also the case for the methylal radical cation, xenon may facilitate the intramolecular H shift to yield a thermodynamically more favorable distonic radical cation:

$$CH_3OCH_2OCH_3^{\bullet +}(Xe) \rightarrow CH_3(OH^+)^{\bullet}CHOCH_3 \quad (10)$$

This mechanism can be also tested by IR spectroscopy due to formation of O−H bond in the reaction product.

The "catalytic" mechanism outlined above may be a common pathway leading to formation of distonic radical cations from primary ionic species in solid chemically inert polarizable matrixes.

5. Conclusion

In the present study, we discussed a remarkable matrix dependence of the trapping and degradation of methylal radical cation in solid rare gases. The observed peculiarities can be rationalized in terms of effects of basic matrix electronic characteristics, such as IP and polarizability, on the cation properties, which appears to be a common way to understand the environment effects on structure and chemistry of organic radical cations. Two consequences may be of specific interest for matrix isolation and general physical organic chemistry. The first one deals with the criteria of matrix choice for stabilization of radical cations produced by high-energy irradiation in solid rare gases. Actually, the probability of trapping of radical cations is generally a matter of compromise between different matrix characteristics (namely, IP and polarizability or basicity). We believe that this limitation may account for a number of puzzling results and failures in attempts to generate average-size primary aliphatic cations in solid rare gases. However, more experimental and calculational work should be done in order to clarify the influence of cation structure and the role of thermodynamic and kinetic factors in observed matrix effects. The second consequence of our results may be a contribution to understanding the fundamentals of matrix-controlled chemistry of the radical cations in condensed phases. We hope that further studies using a combination of EPR and IR spectroscopy will allow us to sort out various mechanistic pathways and to get deeper insight in the solid-state chemistry of highly reactive organic radical cations in matrixes with variable physical characteristics.

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