Fragmentation and Ion–Molecule Reactions of Radical Cations of Diethylmercury as Studied by EPR and UV Spectroscopy

Vladilen N. Belevskii,[a,*] Sergey I. Belopushkin,[a] Michail Ya. Mel'nikov[a] and Vladimir I. Feldman[b]

[a]Department of Chemistry, Moscow State University, Lenin Hills, V-234, Moscow, 119899, Russia and [b]L. Ya. Karpov Institute of Physical Chemistry, 10 Vorontsovo Pole Str., Moscow, 103064, Russia

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The reactions of the radical cations of diethylmercury generated by X-ray irradiation in Freon matrices (Freon-11, Freon-113 and a mixture of Freon-11 and Freon-114B2) at 77 K have been studied by EPR and UV spectroscopy. The radical products of the transformations of the radical cations in liquid diethylmercury at 293 K were characterized by spin trapping techniques using 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) as a spin trap. The electronic absorption spectrum of diethylmercury radical cations measured in a Freon mixture glassy matrix at 77 K exhibits a maximum with well-defined vibronic structure at $\lambda_{max} = 530$ nm $[\varepsilon(\lambda_{max}) = 1.2 \times 10^4$ M^{-1} $cm^{-1}]$. The quantum yield of photoconversion at 546 nm is $\phi = 2.10^{-3}$. The absorption band with $\lambda_{max} \approx 540$ nm remaining in the optical spectrum after complete decay of all the paramagnetic species was ascribed tentatively to $HgEt^+$ cations. The EPR spectra of ethyl radicals were observed mainly for samples in irradiated concentrated solutions of diethylmercury (5–10 vol%) in Freon-11 and Freon-113. It was suggested that ethyl radicals resulted from the fragmentation of 'unrelaxed' radical cations of diethylmercury: $(HgEt_2^{\cdot+} \rightarrow CH_3CH_2^{\cdot} + HgEt^{\cdot})$. The spin adducts of ethyl radicals predominated in the EPR spectra of irradiated liquid solutions of BNB in diethylmercury at 293 K; the adducts of $Me^{-\cdot}CHHgEt$ radicals were also detected in minor concentrations. $Me^{-\cdot}CHHgEt$ radicals were found to result from an ion–molecule reaction of diethylmercury radical cations occurring in a Freon-113 matrix at 110–130 K. Evidence for the formation of the terminal radicals $^{\cdot}CH_2CH_2HgEt$ in this matrix was also obtained.

Organometallic compounds are of biological significance because of their high specific toxicity. In particular, mono- and dialkylmercury derivatives may result from less toxic ionic mercury compounds occurring in industrial waste. These toxic organic compounds are metabolized by living organisms.[1,2] The transformations of dialkylmercury in living organisms may involve both radical and ionic pathways. Generally speaking, the mechanism of metal–carbon σ-bond rupture is a key problem of classical organometallic chemistry. This process is commonly treated as either a homolytic or heterolytic reaction yielding a radical pair or ionic pair, respectively. However, there is also a possibility of one-electron oxidation of an organometallic compound followed by rapid fragmentation of the resulting radical cation, eqn. (1).

$$M\text{-}CR_3 \xrightarrow{-e} M\text{-}CR_3^{+\cdot} \rightarrow M^+ + {}^{\cdot}CR_3 \qquad (1)$$

Okhlobystin[3] has postulated that electron transfer at the initial stage is the main route of organometallic reactions. For a long time, direct detection of the intermediates of one-electron oxidation and investigation of their reactivity was impossible because of the extreme instability of radical cations. In recent years, the EPR technique has been used extensively to study organic radical cations generated in γ-irradiated Freon matrices at low temperatures.[4] Isolated radical cations are trapped in Freon matrices under conditions of high dilution. Variations of additive concentration, temperature and matrix type make it possible to study various transformations of the radical cations. In a recent paper[5] we found that the radical cations of some simple organometallic compounds could be unambiguously identified in frozen Freon matrices. In addition, we have observed the radical
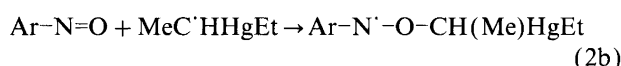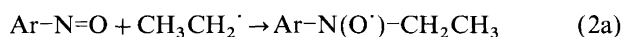
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* To whom correspondence should be addressed.

products resulting from fragmentation and intermolecular interactions of the radical cations. Dialkylmercury radical cations were first studied by Symons et al.[6,7] in CCl_4 and $CFCl_3$ matrices. However these authors obtained no evidence for the formation of alkyl radicals as a result of fragmentation of the radical cations.

In the present work we studied thermal and photochemical transformations of diethylmercury radical cations generated in frozen Freon matrices at 77 K by EPR and optical absorption spectroscopy. Freon-11 ($CFCl_3$), Freon-113 ($CF_2ClCFCl_2$) and a glassy mixture (1:1) of Freon-11 and Freon-114B2 (CF_2BrCF_2Br) were used. In addition, the formation of radicals resulting from the reactions of the primary radical cations in liquid diethylmercury was studied using 2,4,6-tri-tert-butylnitrosobenzene (BNB) as a spin trap. The techniques used in the EPR experiments with Freon matrices[8] and solutions of spin traps[9] have been described previously. All the samples were degassed to a residual pressure of 10^{-4} Torr in SK-4B glass ampoules (for EPR studies) or in synthetic quartz ampoules (for UV studies) and irradiated with X-rays (30 keV) up to doses of 5 kGy (Freon solutions for EPR studies) or 0.5–2 kGy (UV studies) at 77 K, or 100–200 Gy at 293 K (diethylmercury solutions of BNB). Et_2Hg concentration in Freons varied from 0.1 to 10 vol%. EPR spectra were measured with an X-band spectrometer at 77 and 293 K, and in the range 100–160 K. Electronic absorption spectra for samples in glassy Freon mixture matrix (FM) were recorded at 77 K with a Specord M-40 spectrophotometer. Techniques for the measurements of UV–VIS spectra in EPR quartz ampoules (optical path 0.3 cm) have been described previously.[10] The photolysis of X-irradiated samples was carried out using a high pressure mercury lamp (500 W) with a narrow-band filter ($\lambda = 546$ nm).

Results

1. Radiolysis in the liquid phase. Irradiation of a 0.2–0.1 M BNB solution in diethylmercury at 293 K resulted in the formation of the BNB adduct of ethyl radical (Fig. 1). The well-resolved EPR spectrum of this adduct (nitroxyl radical) is a $3 \times 3 \times 3$ multiplet with coupling constants $a^N = 13.7$ G, $a_\beta(2 H) = 18.2$ G due to the methylene protons of added $MeCH_2^\cdot$ radical and $a_m(2 H) = 0.8$ G due to the meta-protons of aryl group. These constants are characteristic of the known BNB adduct of ethyl radical.[11] The fraction of this adduct is about 90% of the total radicals observed in the EPR spectrum of 0.1 M BNB solution irradiated at 293 K. These adducts are stable at 293 K for several days. A minor contribution into the spectrum, a 3×4 multiplet with $a^N = 11.0$ G, $a_\beta(1 H) = a_m(2 H) = 2.0$ G, $g = 2.0040$ (oxyaminyl radicals), results from the addition of a secondary alkyl-type radical, most probably $Me^\cdot CHHgEt$, to the oxygen atom of the BN molecule. It should be noted that no radical adducts of BN were found before irradiation. This implies that the observed adducts result from addition of radiolytically produced radicals to BNB [eqn. (2)].

$$Ar-N=O + CH_3CH_2^\cdot \rightarrow Ar-N(O^\cdot)-CH_2CH_3 \quad (2a)$$

$$Ar-N=O + MeC^\cdot HHgEt \rightarrow Ar-N^\cdot-O-CH(Me)HgEt \quad (2b)$$

The relative concentration of the adducts of $MeC^\cdot HHgEt$ radicals decreases and that of the adducts of ethyl radicals increases with increasing the concentration of BNB. This result is due to the competition between the reactions of ethyl radicals with BNB, eqn. (2a), and diethylmercury, eqn. (3). Thus, the results of the spin-trapping studies indicate that ethyl radicals
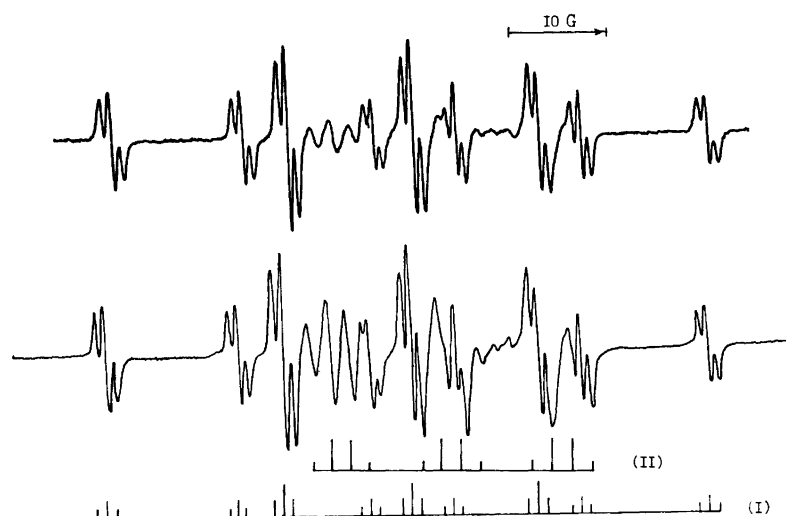

Fig. 1. EPR spectra diethylmercury solutions containing BNB irradiated at 293 K. The concentration of BNB was (a) 0.1 and (b) 0.02 M. I, BNB adduct with $CH_3CH_2^\cdot$ radical; II, BNB adduct with $Me^\cdot CHHgEt$ radical. The spectra were measured at 293 K.
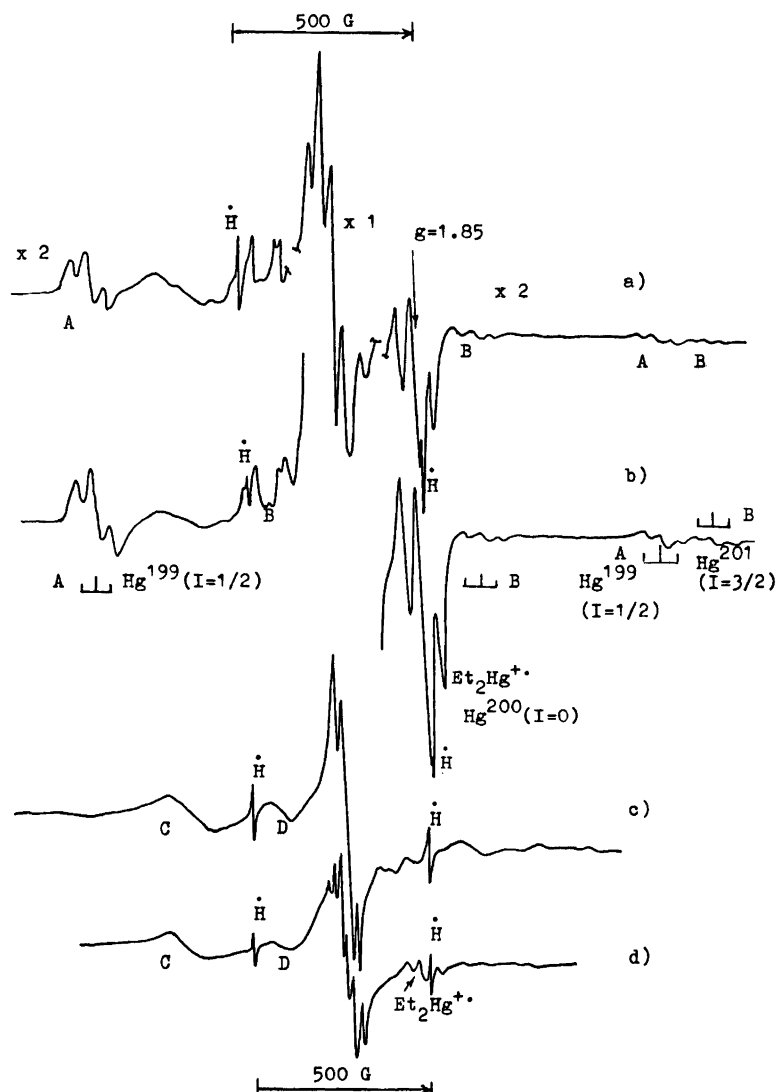
Fig. 2. EPR spectra of Freon solutions of $HgEt_2$ irradiated at 77 K: (a) 0.05% $HgEt_2$ in FM; (b) 5% $HgEt_2$ in FM; (c) 0.5% $HgEt_2$ in Freon-113 after heating to 120 K; (d) 0.5% $HgEt_2$ in $CFCl_3$. The spectra were recorded at 77 K. The features due to splitting by ^{199}Hg ($I = 1/2$) and ^{201}Hg ($I = 3/2$) nuclei are marked A and B, respectively. The central triplet results from ^{200}Hg-containing radicals. Lines D are probably due to splitting by ^{199}Hg in radical $Me\dot{C}HHgEt$.

are major primary radical products of the liquid-phase radiolysis of diethylmercury.

$$CH_3\dot{C}H_2 + HgEt_2 \rightarrow C_2H_6 + EtHg\dot{C}HCH_3 \qquad (3)$$
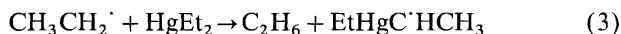
2. Radiolysis of Freon solution. As mentioned above, Symons *et al.*[6,7] obtained no evidence for the fragmentation of the diethylmercury radical cations yielding ethyl radicals in dilute (0.1 mol%) solutions of $HgEt_2$ in Freon-10 (CCl_4) and Freon-11. Meanwhile, our studies revealed that ethyl radicals occur as principal intermediates in the radiolysis of diethylmercury, at least in the liquid phase. In order to learn more about the stability and reactions of diethylmercury radical cations in the condensed phase, we studied the effects of the nature of the Freon matrix and solute concentration on the trapping and properties of the radical cations. In addition, we characterized the

structure and behaviour of electronically excited radical cations by means of UV–VIS spectroscopy.

An FM glassy matrix was found to be best suited for the stabilization of diethylmercury radical cations. Irradiation of an FM solution containing $HgEt_2$ (0.05–5 vol%) resulted in well-defined spectra of the radical cations† (Fig. 2a,b), which are stable for a long time (at least 1 day). The radical cations containing ^{200}Hg isotope ($I = 0$, 70% abundance) show a triplet with $g = 1.85$ (considerably shifted in comparison with $g = 2.003$ for alkyl radicals) and splitting constant $a(2\,H) =$

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† An intense signal of unknown origin is observed in the central region of the spectra measured in an FM matrix (see also Refs. 6, 7); fortunately, this signal does not interfere with the principal features of the EPR spectrum of $HgEt_2^{+\cdot}$ because of the strong, characteristic g-shift for the latter species.

44 G. Symons *et al.*[6,7] assigned this triplet splitting to two specific methyl protons (assuming restricted rotation of the CH_3 groups). An additional doublet of triplets of much lower intensity (features A in the spectrum shown in Fig. 2a) with very large doublet splitting (≈ 1560 G) and similar triplet splitting (44 G) results from the radical cations containing ^{199}Hg ($I = 1/2$, $\mu = 0.498$, 16.84% abundance). Even weaker features (B) observed in the experimental spectrum can be assigned to radical cations containing ^{201}Hg ($I = 3/2$, $\mu = -0.551$, 13.24% abundance).

In Freon-11 matrix the intensity of the signals from diethylmercury radical cations is reduced drastically in comparison with the spectrum observed in an FM matrix. In the case of 0.5% $HgEt_2$ solution in $CFCl_3$, even the major central triplet is of low intensity (Fig. 2d), whereas at higher concentrations of diethylmercury (5–10%) the corresponding lines are completely absent. Irradiation of concentrated solutions (5–10%) of $HgEt_2$ in Freon-11 and Freon-113 produces mainly a quartet of triplets (Fig. 3). The lines of this multiplet are broadened at 77 K (especially in the case of Freon-113), but the resolution improves upon warming the sample to 150 K in Freon-11. The coupling constants of $a(3\ H) = 27.0$ G and $a(2\ H) = 21.0$ G are in accordance with the parameters reported for ethyl radical: $a_\alpha(2\ H) = 22.38$ G,

$a_\beta(3\ H) = 26.89$ G.[12] Generally speaking, line broadening in the signal of this radical may be due to several reasons: restricted motion, interactions with magnetic nuclei of the matrix, etc. However, the signal of ethyl radical produced from the radical cation of propionic acid in the same Freon matrix shows no line broadening of this kind.[13] This implies that the line broadening probably results from some specific reason concerned with the nature of the precursor of the ethyl radical. One possible explanation is that the signal broadening is due to interaction of ethyl radical with HgEt$^+$ ion, which is formed as the counterpart of Et$^\cdot$ in the fragmentation of $HgEt_2^{+\cdot}$ radical cation.

The relative yield of ethyl radical increases remarkably with increasing concentration of diethylmercury in Freon-11 and Freon-113. Irradiation of Freon solutions of intermediate concentration (0.5–2%) gives rise to signals of several radicals, which are poorly resolved at 77 K. In the case of Freon-113, warming the irradiated samples to 110 K (or higher temperatures) results in irreversible changes of the spectrum and partially reversible improvement of the resolution. Well-resolved spectra were recorded for samples in this matrix at 126–133 K. Analysis of these spectra (Fig. 4) makes it possible to identify two radicals.

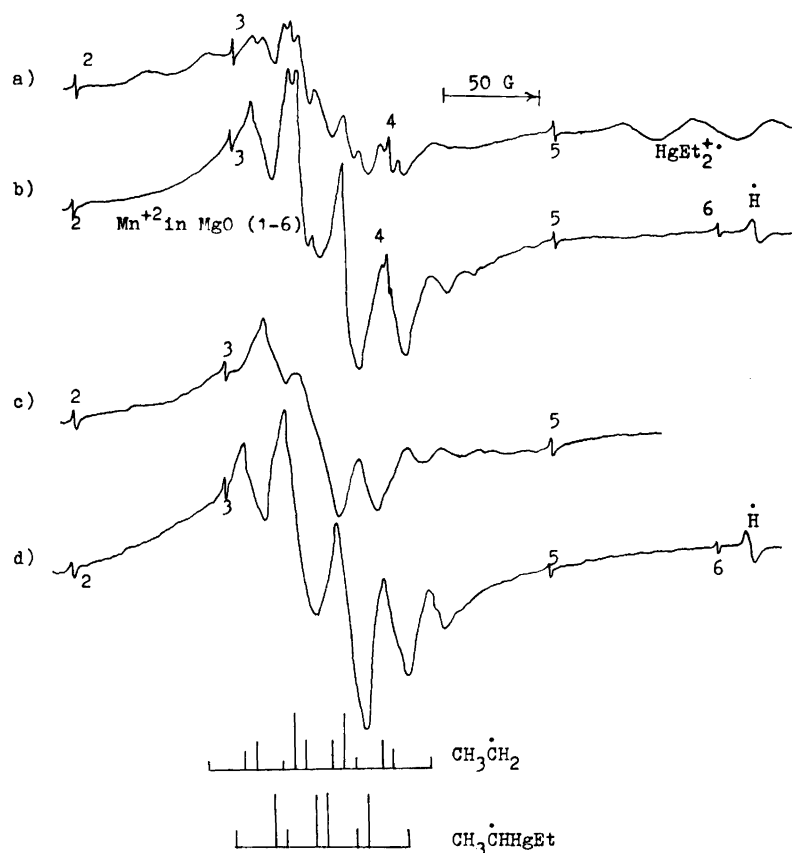A quartet of doublets with coupling constants

Fig. 3. EPR spectra of irradiated frozen solutions of HgEt$_2$ in (a, b) CFCl$_3$ and (c, d) Freon-113. The concentrations of HgEt$_2$ were (a, c) 1%; (b) 10%; and (d) 5%. The field markers are the lines from Mn^{2+} in MgO. All the spectra were taken at 77 K.
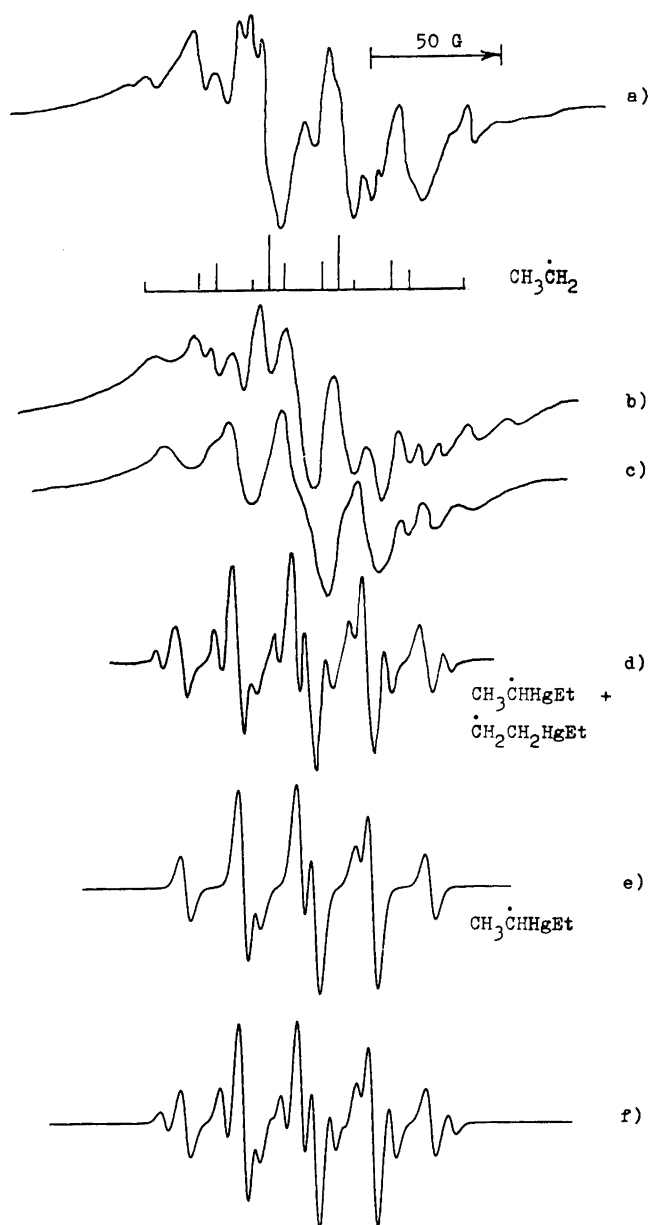
Fig. 4. EPR spectra of frozen Freon solutions irradiated at 77 K and recorded at various temperatures: (a) 10% HgEt$_2$ in CFCl$_3$: the spectrum was measured at 120 K; (b–e) 5% HgEt$_2$ in Freon-113; the spectra were measured at (b) 108, (c) 113, (d) 126, and (e) 133 K; (f) simulated spectra of the mixture of MeC˙HHgEt and ˙CH$_2$CH$_2$HgEt radicals (4:1 ratio; 50% Gaussian linewidths of 2.4 and 2.2 G, respectively, were assumed in the simulation).

$a(3$ H$_\beta) = 22.5$ G and $a(1$ H$_\alpha) = 27.7$ G, which accounts completely for the spectrum observed at the highest temperature (133 K, Fig. 4e), is due to the most stable radical. For both structural and mechanistic reasons, this species should be the MeC˙HHgEt radical. However, the observed coupling constants are not fully consistent with the structure of a planar MeC˙HX-type radical. Indeed, the α-proton coupling constant is expected to be smaller, whereas the methyl proton coupling constant should be

relatively larger [for example, the corresponding values for MeC˙HOH radical are $a(3$ H$_\beta) = 22.22$ G and $a(1$ H$_\alpha) = 15.4$ G, $a(OH) = 1.13$ G.[14] This result may be tentatively explained by a slight pyramidal distortion of the structure of the MeC˙HHgEt radical. Such a distortion should result in some increase in the s-character of the SOMO, which brings about an increase of the α-proton coupling constant and a decrease of the methyl β-proton coupling constant. Effects of this kind have actually been observed for fluorine- and chlorine-substituted alkyl radicals.[15] It is difficult to make a valid conclusion about the formation of MeC˙HHgEt radicals immediately after radiolysis of dimethylmercury in Freon-113 and Freon-11 at 77 K because of poor spectral resolution. Nevertheless, the EPR spectra of irradiated solutions of dimethylmercury in Freon-11 (Fig. 2d) exhibit the broadened features D separated by ca. 430 G, which can be ascribed to the splitting by the [199]Hg isotope nucleus in the MeC˙HHgEt radical [in accordance with the splitting $a($[199]Hg$) = 450$ G in the MeC˙HHgCl radical].[16] Even more pronounced features of this kind were observed in the case of Freon-113 after warming the irradiated sample to 120 K (Fig. 2c).

In addition to the signal of the MeC˙HHgEt radical, six almost equidistant lines with an average separation of ca. 22 G were observed in the EPR spectrum measured in Freon-113 at 126 K (Fig. 4d). These lines disappear completely upon warming the sample to 133 K. We ascribed the sextet spectrum to the terminal alkyl-type radical ˙CH$_2$CH$_2$HgEt assuming a specific conformation of the β-methylene group, which results in the coupling constant with one β-proton approximately twice as large as the coupling constant with other protons: $a(2$ H$_\alpha) \approx a(1$ H$_{\beta 1}) \approx \frac{1}{2} a(1$ H$_{\beta 2})$. More precise consideration using computer simulation resulted in the following coupling constants: $a(2$ H$_\alpha) = 23.0$ G, $a(1$ H$_{\beta 1}) = 22.8$ G, $a(1$ H$_{\beta 2}) = 40.6$ G. According to the so-called $\cos^2 \theta$ rule for β-proton coupling [$a($H$_\beta) \approx B\rho \cos^2 \theta$], these parameters correspond to the conformation of the β-methylene group with dihedral angles of $\theta_1 = 16°$ and $\theta_2 = 44°$. Note that similar conformations have been reported for some 1-alkyl radicals resulting from alkane radical cations in an SF$_6$ matrix.[17] The simulated spectrum of the mixture of MeC˙HHgEt and ˙CH$_2$CH$_2$HgEt radicals (4:1) is shown in Fig. 4f; this spectrum is in good agreement with the experimental spectrum measured in Freon-113 at 126 K (Fig. 4d).

The broadened unresolved lines (Fig. 2c) in low (C) and high fields with splitting about 800 G may be tentatively due to splitting by the [199]Hg isotope nuclei in the ˙CH$_2$CH$_2$HgEt radical in accordance with published data;[18] alternatively they may belong to some other species, e.g. a radical from the matrix.

3. Electronic absorption spectrum and photolysis of diethylmercury radical cation in a glassy FM matrix. The electronic absorption spectra of X-ray irradiated solutions of diethylmercury (0.5–5% vol) in an FM glassy
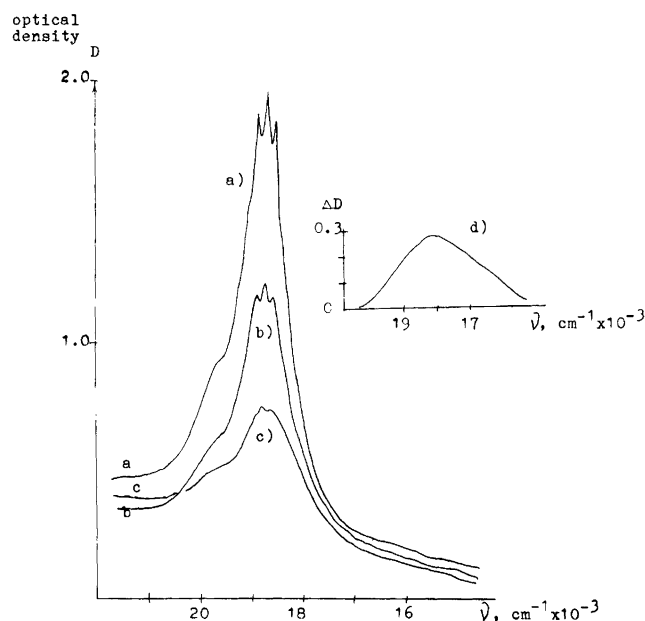
Fig. 5. Absorption spectra of a solution of 5 vol% HgEt$_2$ in FM X-irradiated at 77 K: (a) immediately after irradiatioin at 77 K; (b,c) after subsequent treatment with light of $\lambda =$ 546 nm over (b) 20 and (c) 120 min. (d) Differential absorption spectrum after heating the sample (c) to the temperature of decay of all of the paramagnetic species.
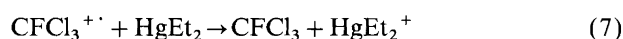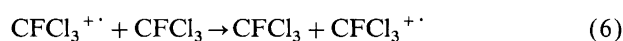
matrix (Fig. 5) exhibit a maximum with well-defined vibronic structure at $\lambda_{max} = 530$ nm. The decay of this absorption band upon photolysis at 546 nm correlates well with the decay of the EPR signal of HgEt$_2^{+\cdot}$, which allows us to assign the absorption with $\lambda_{max} = 530$ nm to diethylmercury radical cations. The molar absorption coefficient for this species can be determined using the concentration of the radical cations estimated from the EPR data. Because the central part of the EPR spectrum is contaminated by a rather strong background signal (see above), we used double integration of the low-field triplet (left-hand A feature in Fig. 2a), corresponding to the ^{199}Hg radical cations, to minimize the error in the determination. The concentration of HgEt$_2^{+\cdot}$ was calculated taking into account the relative abundance of Hg isotopes and *g*-factors (field positions) of the low-field component of ^{199}Hg radical cation and signal of the reference sample.‡ The relative error in the determination of the concentration was estimated to be about 30–40%. The estimated value of the molar absorption coefficient, $\varepsilon(\lambda_{max}) = 1.2 \times 10^4$ M^{-1} cm^{-1}, is rather large, which appears to be a characteristic of radical cationic species. Decay of the absorption of the radical cations is accompanied by a slight high-frequency shift of the absorption maximum and disappearance of the vibronic structure (Fig. 5c). A broad structureless band with $\lambda_{max} = 540$ nm (Fig. 5d) remained in the absorption spectrum after warming of the sample to complete decay of all the

‡ Note that the signal intensity is proportional to g^2.[19] CuCl$_2 \cdot 2$CH$_2$O was used as a reference sample with a known number of spins.

paramagnetic species (as monitored by EPR). This band disappears after melting of the sample, i.e., it is due to some diamagnetically active species. We have tentatively assigned this absorption to HgEt$^+$ cations resulting from the fragmentation of excited radical cations. The total concentrations of paramagnetic species remained virtually unchanged after photoconversion of the diethylmercury radical cations; unfortunately, it was not possible to make a definite identification of the radical products of photolysis because of the overlap of the signals from several radicals in the central region of the spectrum. The quantum yield of bleaching of the diethylmercury radical cations at 546 nm was estimated to be $\phi = 2 \times 10^{-3}$. The low value of the quantum yield may result from multichannel energy degradation in the excited radical cations.

Discussion

The results obtained provide clear evidence for radiolytic fragmentation of diethylmercury both in the liquid phase and in frozen Freon matrices. In order to elucidate the fragmentation mechanism, we consider first the processes occurring in Freon matrices. Since the ionization potentials (E_i) of Freons are considerably higher than that of diethylmercury§ the solute radical cations should be readily formed due to exothermic charge transfer, eqns. (4)–(7).

$$CFCl_3 \rightsquigarrow CFCl_3^{+\cdot} + e^- \tag{4}$$

$$e^- + CFCl_3 \rightarrow CFCl_3^{-\cdot} \rightarrow CF^{\cdot}Cl_2 + Cl^- \tag{5}$$

$$CFCl_3^{+\cdot} + CFCl_3 \rightarrow CFCl_3 + CFCl_3^{+\cdot} \tag{6}$$

$$CFCl_3^{+\cdot} + HgEt_2 \rightarrow CFCl_3 + HgEt_2^+ \tag{7}$$

The fate of the radical cations HgEt$_2^{+\cdot}$ is affected by the nature of the Freon matrix and solute concentration. In the case of FM matrix, the radical cations are quite stable over the whole concentration range studied. However, in the cases of Freon-11 and Freon-113, ethyl radicals predominate in the EPR spectra, especially at higher concentration. A plausible explanation is that the fragmentation occurs from some 'unrelaxed' (excited) diethylmercury radical cations, which are formed at higher solute concentrations in freons, eqn. (8).
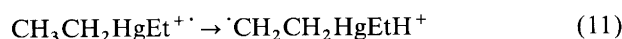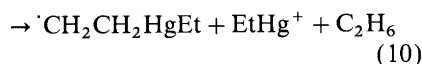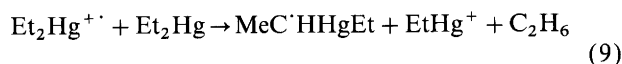
$$(Et_2Hg^{+\cdot}) \rightarrow EtHg^+ + {}^{\cdot}C_2H_5 \tag{8}$$
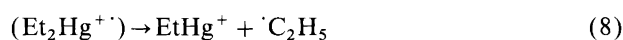
Involvement of excited solute radical cations was postulated in studies of alkanes in SF$_6$[21] and ethers in Freon matrices[22] (the term 'unrelaxed' originates from the work of Iwasaki *et al.*[21] indicating that the nature of excitation is unclear). Generally speaking, the efficiency of excess energy dissipation for the solute radical cation should depend on the cation–matrix interaction, which appears to be stronger in the FM matrix. This may be the cause of remarkable matrix effect on the fragmenta-

§ $E_i = 11.77$, 11.99 and 11.4 eV for Freon-11, Freon-113 and Freon-114B2; $E_i = 8.9$ eV for HgEt$_2$.[20]

tion process observed in the present study. Although the explanation is tentative, we show below that it is somewhat supported by the results of the photochemical studies and the liquid-phase radiolysis experiments. It should be noted that a qualitatively similar effect of the solute concentration on fragmentation processes has recently been observed for the radical cations of trimethylboron, dimethylzinc and diethylzinc generated by γ-irradiation in Freon matrices.[5] The proportion of ˙CH_3 radicals increases with increasing concentration of Me_3B and Me_2Zn. In the case of a 10–20% solution of Me_2Zn, the methyl radical predominates in the EPR spectra. The radical cations of diethylzinc undergo similar conversion.[5] Methyl and ethyl radicals can also result from fragmentation of excited radical cations generated in concentrated solution.

The formation of other radical species in a Freon-113 matrix may be due to an ion–molecule reaction or rearrangement [eqns. (9)–(11)].

$$Et_2Hg^{+\cdot} + Et_2Hg \rightarrow MeC˙HHgEt + EtHg^+ + C_2H_6 \tag{9}$$

$$\rightarrow ˙CH_2CH_2HgEt + EtHg^+ + C_2H_6 \tag{10}$$

$$CH_3CH_2HgEt^{+\cdot} \rightarrow ˙CH_2CH_2HgEtH^+ \tag{11}$$

The secondary radical MeC˙HHgEt is the most stable species, which may also result from the reactions of primary radicals ˙C_2H_5 and ˙$CH_2CH_2HgEt(H^+)$, i.e., reaction (3) and reaction (12).

$$˙CH_2CH_2HgEt(H^+) + Et_2Hg$$

$$\rightarrow MeC˙HHgEt + Et_2Hg(H^+) \tag{12}$$
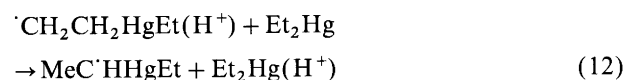
The proposed scheme allows us to explain the results obtained in the studies of the liquid-state radiolysis using the spin trapping technique. First, we should note that the radicals observed in the presence of BNB (spin trap) cannot result from the reactions of solvated electrons or radical anions since virtually all the excess electrons should be scavenged by BNB. Indeed, aromatic nitroso compounds are known to be very efficient electron scavengers [$k(e_{aq} + PhNO) = 4 \times 10^{10}\,M^{-1}\,s^{-1}$)[23] and strong oxidizing agents [one-electron reduction potential of BNB in water $E^{01} = -0.47\,V$ (NHE)];[24] on the other hand, diethylmercury is a covalently bonded species with a high reduction potential ($E^{01} \approx -3\,V$). Even if the radical anions of diethylmercury were formed, they should be readily oxidized by BNB molecules. The presence of BNB in relatively high concentrations (0.02–0.1 M) should result in scavenging of all electrons in the bulk of solution and also of electrons in geminate pairs. This implies that the neutral radicals trapped as BNB adducts result essentially from the primary radical cations of diethylmercury. As shown above, the adducts of ethyl radicals predominate in the EPR spectra of irradiated liquid solutions of BNB in diethylmercury. We may suggest that the formation of these radicals is due to fragmentation of 'unrelaxed' (excited) primary radical

cations [reaction (8)]. In this case, excited radical cations result from direct ionization of diethylmercury molecules in the liquid phase; such behaviour of radical cations is also observed in concentrated frozen solutions of diethylmercury in some Freons. On the other hand, radical cations resulting from distant charge transfer ('indirect ionization') in dilute frozen Freon solutions probably do not possess sufficient excess energy, so the fragmentation does not occur. Similar trends in the behaviour of radical cations in the liquid state and in frozen Freon matrices has been observed previously for aliphatic amides.[9]

An indication of the fragmentation of excited radical cations was also obtained in our photochemical experiments. Although the identification of the products of phototransformation of the radical cations is not straightforward, we have evidence for the formation of a diamagnetic ion, presumably $HgEt^+$ upon photolysis. The low quantum yield of the reaction may be due to efficient deactivation of the excited radical cations resulting from strong cation–matrix interactions in FM matrix (see above).

In conclusion, the properties of diethylmercury radical cations depend crucially on the mechanism of their formation and on environmental effects. The ground-state radical cations are stable in rigid FM matrix. However, 'unrelaxed' (probably, vibrationally excited) radical cations, which are readily formed in the radiolysis of diethylmercury in the liquid phase or in concentrated frozen solutions in Freon-11 and Freon-113, undergo rapid fragmentation to yield ethyl radicals. In addition, the ground-state radical cations may undergo diffusion-controlled ion–molecule reactions in Freon-113 matrix.

References

1. Miller, G. T. *Living in the Environment*, Wadsworth, Belmont, CA 1990, p. 620.
2. Johnson, D. J. and Braman, R. S. *Environ. Sci. Technol.* 38 (1974) 1003.
3. Okhlobystin, O. Yu. *Electron Transfer in Organic Reactions* (in Russian), Izvest. Rostov University, Rostov n/D 1974.
4. Symons, M. C. R. *Chem. Soc. Rev. 13* (1984) 393.
5. Belevskii, V. N., Urtaeva, Zh. Kh., Belopushkin, S. I. and Okhlobystin, O. Yu. *Dokl. Akad. Nauk 325* (1992) 973.
6. Rideout, J. and Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* (1985) 129.
7. Hasegava, A., Rideout, J. and Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* (1990) 637.
8. Belevskii, V. N., Belopushkin, S. I. and Feldman, V. I. *Dokl. Akad. Nauk 31* (1990) 897.
9. Belevskii, V. N. and Belopushkin, S. I. *Khim. Visokich Energii 23* (1989) 133.
10. Gurman, V. S. and Pergushov, V. I. *J. Fiz. Khim. 49* (1975) 1839.
11. Terabe, S. and Konake, R. *J. Chem. Soc., Perkin Trans. 2* (1973) 369.

12. Fessenden, R. W. and Schuler, R. H. *J. Chem. Soc. 39* (1963) 2147.
13. Belevskii, V. N. *Diss. Doc. Sci. (Chem.)*, Moscow State University, Moscow 1990.
14. Livingston, R. and Zeldes, H. *J. Chem. Phys. 44* (1966) 1245.
15. Pschegetskii, S. Ya., Kotov, A. G., Milinchuk, V. K., Roginskii, V. A. and Tupikov, V. I. *ESR of Free Radicals in Radiation Chemistry,* Khimiya, Moscow 1972.
16. Fullam, B. W. and Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* (1974) 1086.
17. Toriyama K., Nunome K. and Iwasaki M. *J. Phys. Chem. 90* (1986) 6836.
18. Symons, M. C. R. and Aly, M. M. *J. Organomet. Chem. 166* (1979) 101.
19. Wertz, J. E. and Bolton, J. R. *Electron Spin Resonance.*

Elementary Theory and Practical Applications, McGraw-Hill, NY 1972.
20. Gurvitch, L. V., Karachevtsev, G. V., Kondrat'ev, V. N., Lebedev, Yu. A., Medvedev, V. A., Popatov, V. K. and Khodeev, Yu. S. *Bond Energy, Ionization Potentials and Electron Affinities,* Nauka, Moscow 1974.
21. Iwasaki, M., Toriyama, K. and Nunome, K. *Radiat. Phys. Chem. 21* (1983) 147.
22. Baranova, I. A., Feldman, V. I. and Belevskii, V. N. *Vestn. Mosk. Univ., Ser. 2: Khim. 42* (1987) 137.
23. Asmus, K. D., Beck, G., Henglein, A. and Wigger, A. *Ber. Bunsenges. Phys. Chem. 70* (1966) 862, 869.
24. Sosonkin, I. M., Belevskii, V. N., Strogov, G. N., Domarev, A. N. and Jarkov, S. P. *Zh. Org. Khim. 18* (1982) 1504.