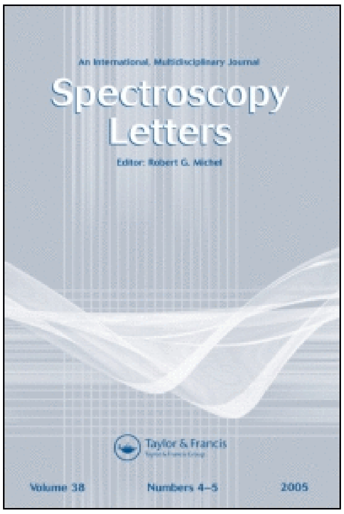

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Search for Pure Compounds Suitable for Use as Matrix in Spectroscopic Studies of Radiation-Produced Radical Cations. II. Perfluoromethylcyclohexane and Perfluoro-Decalin

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To cite this Article Luyckx, Geert , Bosch, Ann Van den and Ceulemans, Jan(1986) 'A Search for Pure Compounds Suitable for Use as Matrix in Spectroscopic Studies of Radiation-Produced Radical Cations. II. Perfluoromethylcyclohexane and Perfluoro-Decalin', Spectroscopy Letters, 19: 3, 207 — 222

To link to this Article: DOI: 10.1080/00387018608069233

URL: http://dx.doi.org/10.1080/00387018608069233

SPECTROSCOPY LETTERS, 19(3), 207-222 (1986)

A SEARCH FOR PURE COMPOUNDS SUITABLE FOR USE AS MATRIX IN SPECTROSCOPIC STUDIES OF RADIATION-PRODUCED RADICAL CATIONS. II. PERFLUOROMETHYLCYCLOHEXANE AND PERFLUORODECALIN.

Radical Cations; Electronic Spectra; Matrix Effects.

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ABSTRACT

A study is made of the suitability of perfluoromethylcyclohexane and perfluorodecalin as matrix in electronic spectroscopy of radiation-produced radical cations, using alkane radical cations as test ions. The intrinsic absorption of the irradiated pure matrices is small and not very photosensitive. Alkane radical cations are produced in good yields by gamma-irradiation and may be eliminated selectively by illumination, thus enabling the observation of pure electronic spectra

0038-7010/86/1903-0207$3.50/0

of these cations by difference spectrometry. The bleaching threshold of octane radical cations is found to be situated at 2.0 eV in both matrices and bleaching is in all likelihood due to photodissociation. The energy level of the positive hole conduction band is quite high in these matrices, making them especially suitable for spectroscopic studies of molecular cations of compounds with high ionization energies.

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Radical cations resulting from ionization of neutral molecules may be produced by gamma-irradiation and stabilised in solid matrices at low temperature, thus allowing their study by spectroscopic techniques. Electronic spectra of such radical cations yield information on excited states of a rather special nature. The removal of an electron from the highest occupied molecular orbital (HOMO) creates the possibility of transitions, induced by light absorption, from lower occupied molecular orbitals to the half-filled orbital. The resulting absorption bands and excited states clearly have no direct counterpart in the neutral molecule. The observed absorption spectra may yield information on the spacing of the energy of the different occupied molecular orbitals that will be comparable to information obtained from photoelectron spectroscopy. Matrix effects should either be absent or clearly understood, so that the exact contribution of these matrix effects to the total energy transition is known. This may require the study of these radical cations in a considerable number of different matrices.

Electronic spectra of radiation-produced radical cations have been obtained in only a rather limited number of different pure compounds and mixtures. Pure compounds used as matrices in such studies have long been limited to a few saturated hydrocarbons[1,2], n- and sec-butylchloride[3,4] and carbon tetrachloride[5]. This series has recently been extended with freons such as 1,1,1-trichlorotrifluoroethane[6] and 1,1-difluorotetrachloroethane[7]. Mixtures of some of these compounds and a freon mixture (an equivolume mixture of CCl_3F and CF_2BrCF_2Br) have also been employed[8-11]. For many purposes, the use of pure compounds as matrices is certainly to be preferred. The number of compounds suitable for use as matrix in spectroscopic studies of radiation-produced radical cations is very strictly limited by nature, however, because of the requirement of positive hole migration. Also, tested matrices may be inadequate for specific studies for different reasons, such as insufficient solubility of the additive compounds or insufficient inclusion in the solid matrix, interference of matrix absorption bands with electronic absorption bands of radical cations studied or insufficient trapping of positive holes on the radical cations studied due to too low a level for positive hole migration in the solid matrix.

Perfluorocarbons are likely candidates for use as matrices, because of the absence of hydrogen atoms in these molecules and thus of proton transfer reactions that could prohibit positive hole migration. In this work, a study is made of the suitability of perfluoromethylcyclohexane and perfluorodecalin for use as matrix in studies of electronic spectra of radiation-produced radical cations, using alkane cations as test ions. The interference of matrix absorption bands is investigated and information is gathered by bleaching experiments on the energy level required for positive hole migration in these matrices.

EXPERIMENTAL

The experimental procedure was largely as described before[6]. Perfluoromethylcyclohexane, perfluorodecalin and n-octane were obtained from Aldrich, 3-methylhexane from K&K and 3-methyldecane from Pfaltz and Bauer; 3-methylheptane, 3-methyloctane and 3-methylnonane were Fluka products. All these products were used as received. Samples were irradiated to a dose of

7.5 10^{19} eV.g^{-1} and 1 mm cells were used in all cases. Actual path lengths at 77 K were determined using azulene solutions. Bleachings were performed by passing the condensed light from a quartz halogen lamp (Sylvania, 250 W) through different cut-off filters onto the sample, maintained at liquid nitrogen temperature. Wavelength thresholds reported for the cut-off filters employed are at 0.5% transmission, whereas photon cutoff energies were taken at 10% transmission. The steepness of the cut-off filters employed was such that differences between photon energies at 2% and 50% transmission were all situated between 0.04 and 0.11 eV.

RESULTS

Irradiation of solid perfluoromethylcyclohexane results in the appearance of an optical absorption that gradually increases towards shorter wavelengths from its high wavelength onset at about 900 nm. Illumination during 40 minutes with wavelengths greater than 610 nm causes the disappearance of a small broad and structureless absorption and the residual absorption spectrum is shown in Figure 1. Further illumination with these and even higher photon energies (for instance 150 minutes with wavelengths greater than 490 nm) has no significant further effect on the spectrum of the irradiated pure matrix. Addition of oc-

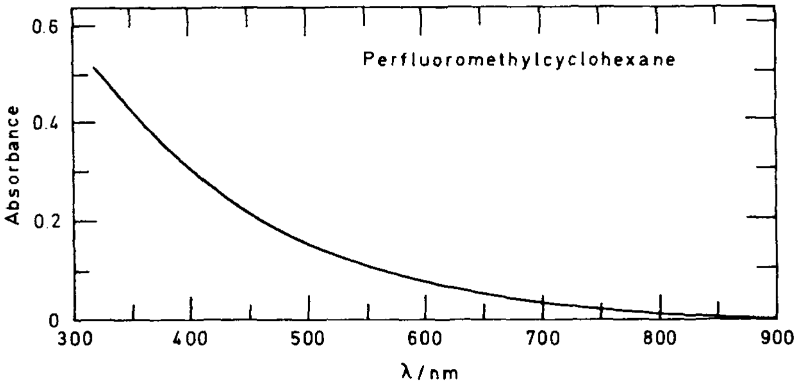

FIG. 1 Absorption spectrum obtained by irradiation and subsequent illumination with wavelengths greater than 610 nm of solid perfluoromethylcyclohexane at 77 K.

tane before irradiation results in the appearance of an important new absorption band around 600 nm. The spectrum obtained after irradiation and after illumination during 40 minutes with wavelengths greater than 610 nm is shown in Figure 2. Subsequent illumination during 150 minutes with wavelengths greater than 490 nm results in the selective elimination of the 600 nm band so that a pure spectrum of this band can be obtained by difference spectrometry. Quite similar results are obtained with perfluorodecalin and these are therefore not discussed in detail. Electronic absorption spectra of a number of 3-methylalkane radical cations in perfluoromethylcyclohexane are shown in Figure 3.

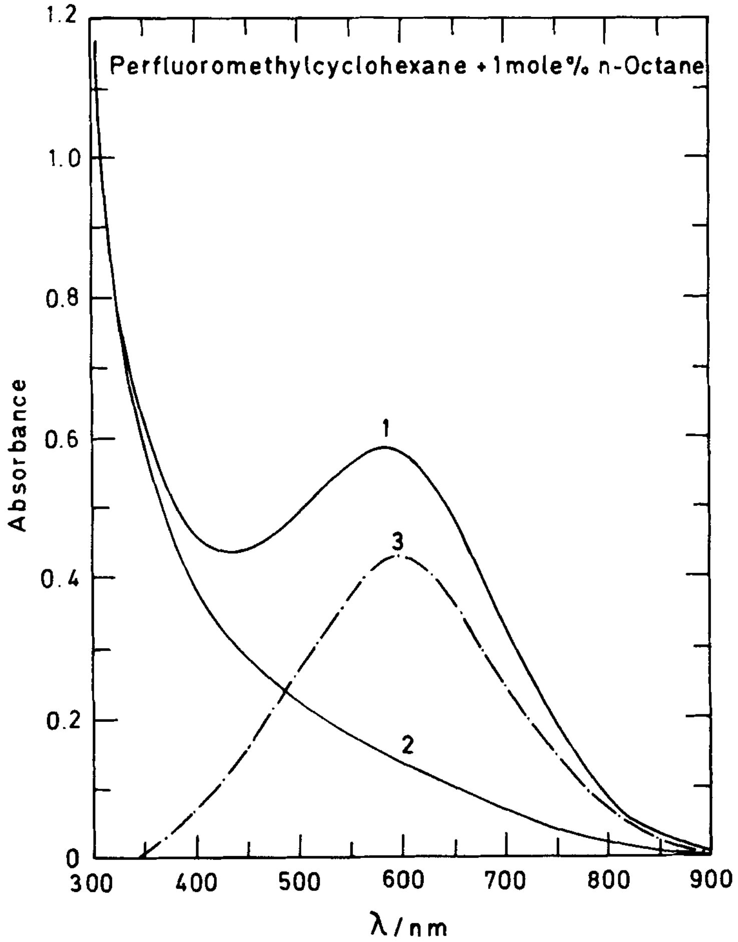

FIG. 2 Absorption spectra obtained by irradiation and successive illuminations with wavelengths greater than 610 nm (1) and 490 nm (2) of perfluoromethylcyclohexane containing 1 mole % n-octane and corresponding difference spectrum (3).

The bleaching threshold of octane radical cations in perfluoromethylcyclohexane and perfluorodecalin may be determined by illumination with gradually in-

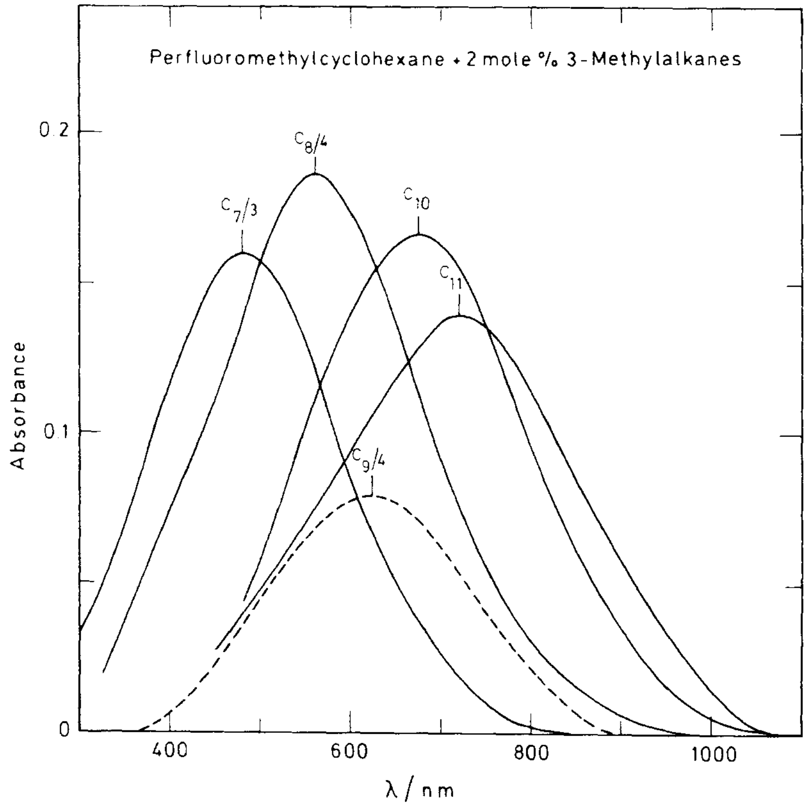

FIG. 3 Electronic absorption bands of 3-methylalkane radical cations in perfluoromethylcyclohexane. Concentration of alkane additives is 2 mole % in all cases. Please note that the absorbance in the case of 3-methylhexane and of 3-methylheptane and 3-methyloctane has been divided by respectively 3 and 4 for convenience of display.

creasing photon energies. Results obtained in perfluoromethylcyclohexane are shown in Figure 4 and indicate that the bleaching threshold is situated at 2.0 eV. The bleaching threshold is thus well within the electronic absorption band and certainly does not correspond

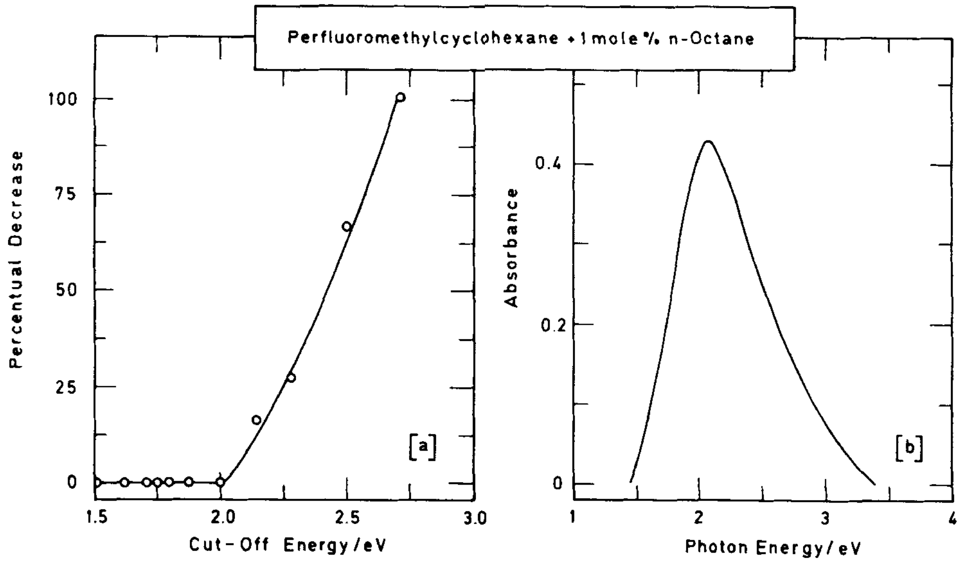

FIG. 4 (a) Percentual decrease in absorbance due to photobleaching of octane radical cations in perfluoromethylcyclohexane versus photon cut-off energy. (b) Absorption spectrum of octane radical cations in perfluoromethylcyclohexane on an energy scale.

with the onset of this band. Results obtained in perfluorodecalin are quite similar and the bleaching threshold is also situated at 2.0 eV.

Quantitative information on hole trapping by alkane additives in perfluoromethylcyclohexane and perfluorodecalin matrices was obtained using 3-methyloctane. An extinction coefficient of 5.2 x 10^3 M^{-1} cm^{-1} has been obtained for 3-methyloctane radical cations by hole competition studies with pyrene[12]. The required absorbances are obtained from bleaching experiments and are considerably more accurate than those simply derived from spectra recorded after irradiation. The radiolytic yield of 3-methyloctane cations -(number of cations formed per 100 eV energy absorbed by the additive)- depends on the additive concentration and matrix employed and a full report on this will be given at a later date. It is already evident, however, that in both matrices yields are obtained that very considerably exceed the maximal yield possible without hole transfer from matrix to additive molecules.

DISCUSSION

Radical cations of alkane additives (A) may be formed by γ-irradiation and stabilised in suitable solid matrices (M) according to the following reaction scheme :

$$\mathrm{M} \rightsquigarrow \mathrm{M}^{+} + e^{-} \qquad (1)$$

$$\mathrm{M}^{+} + \mathrm{M} \longrightarrow \mathrm{M} + \mathrm{M}^{+} \qquad (2)$$

$$\mathrm{M}^{+} + \mathrm{A} \longrightarrow \mathrm{M} + \mathrm{A}^{+} \qquad (3)$$

$$e^{-} + \mathrm{M} \longrightarrow \mathrm{M}^{-} \qquad (4a)$$

$$\longrightarrow \mathrm{B} + \mathrm{C}^{-} \qquad (4b)$$

Ionization by irradiation with gamma rays is a non-selective process; thus, direct ionization of the additive by the ionizing radiation is negligible. Efficient formation of additive cations depends on the occurence of positive hole migration in the matrix (reaction 2) and on the occurence of hole transfer to the additive (reaction 3). The energy level of (the bottom of) the positive hole conduction band is an important parameter in this regard. For the formation and stabilisation of radical cations of molecules with high ionization energies (e.g. alkanes), matrices must be employed for which the energy level of the positive hole conduction band is very high. Results obtained in this work show that the bleaching threshold of octane radical cations in perfluoromethylcyclohexane and perfluorodecalin is situated at 2.0 eV, indicating that the trap depth of positive holes on octane cations in these matrices is at least this high. A threshold of 2.0 eV is also observed for octane radical cations in perfluorohexane. The bleaching threshold is thus independent of the perfluorocarbon matrix used, suggesting that this threshold corresponds with the dissociation threshold of octane radical cations in solid matrices and that the trap depth of positive holes is even higher.

The stability of trapped cations also critically depends on the trapping or scavenging of electrons formed in the ionization process. For glassy systems, physical trapping can be an efficient process for electron stabilization[13]. Efficient scavenging may be the result of electron attachment (reaction 4a) or dissociative electron attachment (reaction 4b) by matrix molecules. Experimental data on electron attachment by saturated perfluorocarbons consistently support the idea that electrons formed in the ionization process are efficiently scavenged by matrix molecules in this study. Electron attachment rates have been measured at high pressures in swarm experiments for trace amounts of a number of perfluorocarbon compounds in mixtures with N_2 and Ar[14-16]. Measured values are large in most cases and depend strongly on structure. For saturated perfluorocarbons, an increase in molecular size (chain length) increases the attachment rate; the cyclic nature of perfluorocycloalkanes, on the other hand, appears to increase greatly the electron attachment cross section. The electron scavenging property of saturated perfluorocarbons in condensed systems has been evidenced by a study of the depression of the hydrogen yield upon their addition in the radiolysis of n-hexane[17]; the effect has conclusively been attributed to interference with ion-neutralization through electron attachment. The depression of the radiolytic hydrogen yield is virtually non-existent for CF_4, C_2F_6 and C_3F_8, it becomes noticeable for n-C_4F_{10} and increases gradually for n-C_5F_{12} and n-C_6F_{14}, being especially pronounced in the case of perfluorocycloalkanes. This clearly fits the pattern observed in gas-phase reactions between electrons and saturated perfluorocarbons. The electron scavenging property of perfluorodecalin in condensed systems has been evidenced by a comparison of its efficiency for quenching geminate-ion recombination fluorescence of saturated hydrocarbon liquids with its efficiency for quenching the fluorescence of these liquids when excited with 165-nm light[18]. The addition of an extra electron to saturated perfluorocarbons has been studied from a theoretical point by Liebman[19].

Negative ions resulting from electron attachment to saturated perfluorocarbons have been studied by several workers. In low pressure mass spectrometric studies, only fragment anions are observed for CF_4, C_2F_6 and C_3F_8, F^- being the most abundant. For n-C_4F_{10} a weak parent anion is observed, but again the predominant ion is F^-. For i-C_4F_{10}, n-C_5F_{12} and n-C_6F_{14} the parent negative ions are the most abundant[20]. In high-pressure swarm studies, dissociative electron attachment appears to be the only negative ion forming process for CF_4 and C_2F_6, but electron attachment occurs to C_3F_8, n-C_4F_{10} and n-C_5F_{12} to give the parent negative ions[16]. In low-pressure mass spectrometric studies of perfluorocycloalkanes, parent anions are generally observed but their abundance is strongly dependent on molecular structure[21]. Low-energy electron impact at 300 K results in a predominance of parent anions in the case of perfluoro-1,2-dimethylcyclobutane and perfluoromethylcyclohexane, but in a predominance of fragment anions for perfluoro-1,1-dimethylcyclopentane. The fraction of parent anions decreases with electron energy and temperature, while those of the fragment anions increase.

ACKNOWLEDGMENTS

The authors wish to thank the Nuclear Center of Mol for financial support. One of us (A.V.d.B.) thanks the I.W.O.N.L. (Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw) for a scholarship.

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Received: 9/28/85

Accepted: 10/28/85