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Photodissociation of Vinyl Chloride: Formation and Kinetics of Vinylidene $H_2CC(^3B_2)$

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The primary photodissociation processes in the photolysis of vinyl chloride have been investigated by using the flash photolysis–kinetic spectroscopic technique. Concentrations and temporal profiles of product $H_2CC(^3B_2)$, HCl, and C_2H_2 are monitored by their absorption in the vacuum ultraviolet at 137, 139, and 151 nm, respectively. HCl and $H_2CC(^3B_2)$ are formed with the same time history via a 1,1 elimination from excited C_2H_3Cl. Rate constants for the interaction of $H_2CC(^3B_2)$ with He, $1.07 \pm 0.17 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, and C_2H_3Cl, 3.5×10^{-11} cm^3 molecule^{-1} s^{-1}, have been obtained.

Introduction

An extensive review article would be necessary to justify a comprehensive listing of the experimental results on the subject of the photolysis of the chloroethylenes. Even limiting the references to those involving vinyl chloride, the molecule of our immediate interest, is not straightforward. If we focus upon those studies involving the ultraviolet dissociation of vinyl chloride and omit the multiphoton infrared laser dissociation studies,[1] we find a variety of experimental approaches. In the absorption region corresponding to the $\pi^* \leftarrow \pi$ excitation (165–220 nm),[2] broad-band photolysis in conjunction with product analysis and use of radical scavengers[3,4] has established the occurrence of two independent primary processes, i.e.

$$C_2H_3Cl \rightarrow C_2H_3 + Cl \qquad (1)$$

$$C_2H_3Cl \rightarrow C_2H_2 + HCl \qquad (2)$$

with a ratio R_1/R_2 of 1.3 independent of temperature (−78–40°) and pressure (2–600 torr). These results were obtained under conditions of relatively high pressures of C_2H_3Cl (up to 600 torr) without rare gas diluent. HCl production through process 2 may involve either a 1,1 or a 1,2 elimination mechanism. In the presence of radical scavengers, the importance of the two elimination processes may be examined by investigation of the product acetylenes from photolysis of CH_2CDCl between 200 and 220 nm. The experiments indicate the C_2H_2/C_2HD ratio is 1, i.e., the 1,1 and 1,2 processes are about equal[4] in importance. The ultraviolet dissociation result is to be compared with results of the infrared multiphoton dissociation experiments, which primarily involve dissociation from the ground electronic state, where a 1,1 elimination of HCl is the predominant elimination channel (2).[5]

Emission from vibrationally excited HCl[2] produced by the broad-band flash photolysis of vinyl chloride at wavelengths greater than 155 nm indicates that, at least during the photolytic excitation process, HCl ($v'' \leq 4$) is a photoproduct. ArF excimer laser excitation (193 nm) of C_2H_3Cl further indicates that not only is the HCl vibrationally and rotationally excited, but emission in the 1100–1300 cm^{-1} region attributable to the bending mode of vinyl radical is also observed.[6] This assignment is based upon similarity in emission from the F + C_2H_4 system.[7]

As noted above, the elimination of HCl as a photoproduct from C_2H_3Cl may produce either a vinylidene radical, by a 1,1 elimination, or acetylene by a 1,2 elimination. In the analogous molecule, C_2H_4, absorption due to triplet vinylidene recently has been observed following the flash photolysis of the substrate in the wavelength region above 155 nm.[8] The role and importance of the vinylidene species in a wide variety of chemical systems has not, to the present, been identified. Triplet vinylidene has been directly observed in several hydrocarbon systems and certain of its properties have been noted previously (ref 8 and references therein). Further, the structure of an excited C_2H_2, often invoked in photochemical systems, has been shown to be identical with that of $H_2C{=}C$.[9] Our recent investigations of the vinylidene radical make a reexamination of the vinyl chloride photodissociation an appealing candidate for a variety of reasons. The presence of vinylidene may be deduced a priori since a 1,1 elimination of HCl has been observed previously and, further, the many possible decomposition fragments arising from a variety of suggested primary processes have strong, well-characterized easily detectable absorptions in the vacuum ultraviolet. Although the vinyl radical has been observed only in the visible spectral region[10] both the $Cl(^2P^0{}_{3/2})$ and the $Cl(^2P^0{}_{1/2})$ at 134.7 and 135.2 nm, respectively, are observable and represent the other moiety from process 1. Similarly, acetylene in its ($\tilde{C}$–$\tilde{X}$) system at 152 nm, $^3B_2(H_2CC)$ at 137 nm, and HCl by absorption to its C state at 129 nm serve to monitor the fragments from process 2. Vinyl chloride in its ground state can be monitored conveniently at 149 nm.

We describe here experiments in which time-resolved absorption measurements in the vacuum ultraviolet by the various photoproducts from vinyl chloride are reported. These results are obtained by using low concentrations of substrate in helium and suggest that another channel, the production of triplet vinylidene, is dominant under our experimental conditions. There is no evidence for singlet vinylidene formation. The nature of the dissociation process and the lifetime of the vinylidene precursor, presumably vinyl chloride in its triplet (π–π^*) state, are discussed.

Experimental Section

The purity of the vinyl chloride, obtained commercially, was checked both by gas chromatography using a flame-ionization detector and by vacuum ultraviolet absorption spectroscopy. Thorough degassing and trap-to-trap distillations reduced impurity

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levels to less than the minimum detectable by either technique. The purified vinyl chloride was premixed with ultrahigh purity helium (99.99%) and expanded into a quartz reaction vessel. Additional inert gas diluent, if necessary, was added directly to the reaction cell and the experiment delayed to allow for the thorough mixing. The mixing time was experimentally determined by chromatographic analysis, i.e., when repetitive sample injections of a typical hydrocarbon–helium mixture resulted in constant peak areas. For example, at 700 torr of He a mixing time of 12 min was necessary. The required mixing time was modified depending upon the particular inert gas and its pressure. In a typical experiment, the final composition was 30 mtorr of vinyl chloride in varying pressures of helium (7–30 torr).

The vacuum ultraviolet flash photolysis–kinetic spectroscopy apparatus has been described previously.[8] A quartz photolysis cell was placed inside a chamber in which a bank of six capacitors, each connected to an electrode pair, were discharged through N_2. The discharge dissipated about 2500 J. Although the active photolysis region, for vinyl chloride, is between 155 and 220 nm, the flash duration was monitored in the visible and indicated a fwhm flash profile of 5 μs.

Spectroscopic analysis was performed with a Garton-type analysis flash (2-μs pulse width) triggered at preset delay times with a photomultiplier–oscilloscope circuit. The vacuum ultraviolet output of the analysis flash was focused, through LiF optics, onto the slit of a 2-m Eagle mount spectrograph whose dispersion was 2.8 Å/mm in first order. Spectra were recorded on vacuum ultraviolet sensitive plates.

Wavelength calibrations were obtained either from one of several strong, well-characterized atomic emissions from the analysis lamp or by absorption of stable molecules such as CO. In practice, a single flash through a 30-μm slit produced adequate plate darkening for densitometric analysis. Concentration data were obtained from the plate transmission and the characteristic curve of the plate response.

HCl and C_2H_2 concentrations were determined on an absolute basis by calibration of the complete optical system against known quantities of the gas. In neither case were the strong absorptions by HCl or C_2H_2 at 129 or 152 nm, respectively, obscured by the substrate mixture.

Results and Discussion

The flash photolysis of vinyl chloride involves the absorption process followed by dissociation of the photolyzed substrate molecules. Upon photolysis, there is an immediate reduction in the ground-state vinyl chloride concentration which accounts for fully half the initial concentration of 30 mtorr. The reduced concentration remains invariant, within experimental error, over the time of the experiment. The observed products and their concentrations, therefore, are not the result of chemical interactions with vinyl chloride, and there is no secondary chemistry which requires invoking interaction between an undetected intermediate with the substrate.

Figure 1 shows the time history of the products and intermediates which include HCl, C_2H_2, and triplet vinylidene radicals. At the shortest delay times, the absence of products is most noticeable. Not shown in Figure 1 is the immediate sharp decrease in parent absorption following the flash. The absence of concurrent product formation strongly suggests involvement of a spectrally inactive or weakly absorbing species. The properties and identification of the "primary" intermediate will be discussed subsequently.

The most favorable thermochemical pathway in the photodissociation of vinyl chloride is the elimination of HCl as in (3)

$$C_2H_3Cl \rightarrow C_2H_2(X^1\Sigma^+_g) + HCl(X^1\Sigma^+) \qquad (3)$$

where the overall ΔH = 23.6 kcal/mol based upon $\Delta H_f(C_2H_2)$ = 54.2, $\Delta H_{f,0}(HCl)$ = −22.1, and $\Delta H_{f,0}(C_2H_3Cl)$ = 8.5 kcal/mol.[11] Since process 3 is expected to occur from the initially photochemically populated excited singlet, the production of either HCl or C_2H_2 in their singlet ground states at short times following the incident flash is a measure of the probability of (3). The minimum detectable quantity of either HCl or C_2H_2, in the present experimental arrangement, is about 1 mtorr. The final concentrations of HCl, independent of initial He pressure between 7–28 torr, is 15 mtorr. Since these products are not observed at short times following the flash, process 3 represents, therefore, no more than 5% of the vinyl chloride photodissociation.

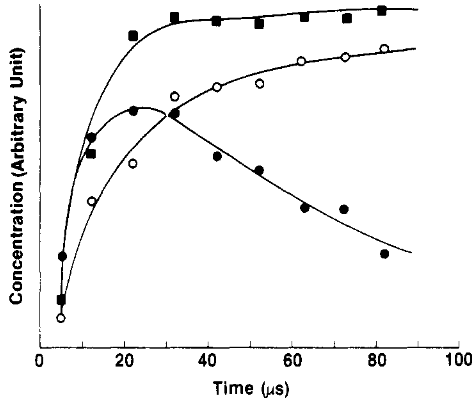

Figure 1. Temporal profile of products. Initial conditions: 30 mtorr of C_2H_3Cl, 28 torr of He; ■, HCl, ○, C_2H_2, ●, $H_2CC(^3B_2)$. Lines are drawn through the experimental points for clarity of presentation.

We cannot, a priori, eliminate the formation of $HCl_{v>0}$ ($X^1\Sigma^+$) as a primary process. However, vibrational relaxation is a very slow process on our time scale, particularly with He as the major and vinyl chloride as the minor collision partner, and would not be expected to contribute to the observed chemistry. Available quenching rates predict a total quenching 1/e time of 7.3×10^{-3} s[2,12] which is several orders of magnitude too slow to be important. Berry[2] has observed laser emission from $HCl_{v>0}$ as the result of $CH_2{=}CHCl$ photolysis with about 25% of the total HCl formed in $v = 0$. The laser emission was observed during the incident flash and within 5 μs after the initiation of the flash. The nonstatistical distribution of energy in vibronic states of HCl relaxes very rapidly within the tail of the flash itself (about 5–10 μs). Our quantitative measurements of the HCl yield at the shortest delay times after the flash (10 μs) indicate that less than 10% of photolyzed C_2H_3Cl has produced HCl which our time scale is mainly in the $v = 0$ level. The laser process is complete prior to our initial observations, and production of HCl by that mechanism is included in the HCl observed at the shortest time.

It was previously noted that HCl can be formed by either a 1,1 or a 1,2 elimination. In the case of a 1,1 elimination, the most energetically favorable path will produce vinylidene in its ground $^1A_1$ state. Since $H_2CC(^1A_1)$ rearranges to C_2H_2 in 10^{-11} s, the absence of C_2H_2 at the shortest delay time is indicative also of the absence of $H_2CC(^1A_1)$.[8] In the case of a 1,2 elimination, the C_2H_2 and HCl temporal profiles will be the same. It is clear from Figure 1 that such is not the case and this is indication that a 1,2 elimination as in process 3 is a minor pathway in the photodissociation.

In terms of the overall energetics, the next most likely primary process involves a C–Cl bond rupture where ΔH = 89 kcal/mol ($\Delta H_f(C_2H_3)$ = 68.4[13] and $\Delta H_f(Cl)$ = 29.1 kcal/mol).[11]

$$C_2H_3Cl \rightarrow C_2H_3 + Cl \qquad (1)$$

In fact, a very weak Cl atom absorption could be detected at 134.7 nm ($^2P^0_{3/2}$–$^2P_{3/2}$). There was no evidence for production of Cl($^2P^0_{1/2}$). We cannot state with certainty the relative importance of process 1. However, we have been able to observe, in another study, Br atoms in both the $^2P^0_{3/2}$ and $^2P^0_{1/2}$ states when produced as a major photoproduct.[14] The oscillator strengths of both Cl

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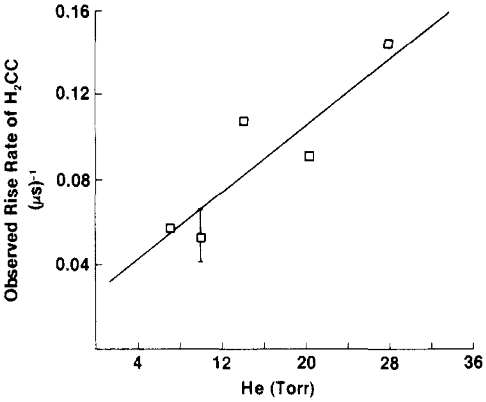

Figure 2. Observed rate of rise of $H_2CC(^3B_2)$ as a function of helium pressure. The error bars are typical experimental errors derived from an analysis of all uncertainties and errors in the measurement.

TABLE I: Slopes of $H_2CC(^3B_2)$ and $HCl(^1\Sigma^+)$ Temporal Profiles

	H_2CC rise	H_2CC decay	HCl rise
μs^{-1} torr^{-1}	0.0039 ± 0.0013	0.000 34 ± 0.000 05	0.003 63 ± 0.000 26
cm^3 molecule^{-1} s^{-1}	(1.2 ± 0.4) × 10^{-13}	(1.07 ± 0.17) × 10^{-14}	(1.12 ± 0.08) × 10^{-13}

transitions, i.e., from the $^2P^0_{3/2}$ or $^2P^0_{1/2}$, are close to equal, and they are slightly larger than the strengths of the comparable Br atom transitions.[15] In neither case were the Cl lines obscured by parent vinyl chloride absorption.

Loss of Cl atoms by reaction prior to spectroscopic observation is unlikely on the experimental time scale. The most probable reaction, that with vinyl chloride, has a rate constant of 2.6 × 10^{-11} cm^3 molecule^{-1} s^{-1}.[16] With a vinyl chloride concentration of 15 mtorr following the flash a $1/e$ time of 80 μs is obtained. Even so, as noted above, the vinyl chloride concentration remains invariant over the time of the experiment further corroborating the relative unimportance of Cl atom production.

Wijnen and co-workers[3] suggest process 1 is the major pathway in the photodissociation of vinyl chloride. The incident energy used in that work (200–220 nm) would surely populate the $^1(n,\sigma^*)^2$ from which rapid dissociation into products would occur. The present work is not comparable as the major absorption here probably occurs in the region of 180 nm where the excited state is the $^1(n,\pi^*)$. Also, in the present work, a large excess of He has been added to minimize any temperature excursions associated with the incident flash photolysis.

Although primary photolytic production of $H_2CC(^1A_1)$ has been eliminated from consideration, results shown in Figure 1 suggest that $H_2CC(^3B_2)$ is formed in the photolysis. The most reliable value for the vinylidene singlet–triplet splitting ($^1A_1$–$^3B_2$) is 42.0 kcal/mol[17] which together with $\Delta H_f(H_2CC)(^1A_1)$ = 100 kcal/mol[18] suggests an overall endothermicity of 111.4 kcal/mol for a dissociation as in (4). Though energetically accessible, the

$$C_2H_3Cl \rightarrow H_2CC(^3B_2) + HCl(^1\Sigma^+) \qquad (4)$$

dissociation to produce triplet vinylidene and $HCl(^1\Sigma^+)$ is spin forbidden from a singlet precursor. The lowest energy triplet of vinyl chloride (π–π^*), 4.0 eV,[19] is well within the photolytic energy range.

There is a pronounced effect of pressure on the temporal history of the observed products. As the pressure of He is increased from 7 to 28 torr, the rise times of the vinylidene and HCl are reduced. The observed H_2CC temporal history was best represented as double exponential, a rapid rise and slower decay. After separation of the two components, the production and decay of $H_2CC(^3B_2)$ were each fit to single exponential curves. The dependences of the rise and fall times on the He pressure were evaluated and are shown in Figures 2 and 3. The slopes derived from these plots and those derived for the rise time of HCl are summarized in Table I. It is clear the rise times of $H_2CC(^3B_2)$ and HCl are the same within the error of one standard deviation derived from the least-squares fit. The possibility was considered that the temporal behavior of both HCl and H_2CC ($^2B_2$) was indicative of relaxation from excited vibrational states produced by the photolysis. The respective rise times would reflect the quenching rates of the two species. The measured rise times, being identical, would require identical deactivation rate coefficients which was considered highly unlikely on the basis of the disparate nature of the two fragments. Bellas et al.[20] have observed only a small effect of pressure from 10 to 200 torr on the $Hg(6^3P_1)$ photosensitized dissociation of vinyl chloride at 600 K. From the small pressure dependence, they have obtained an approximate lifetime of $(C_2H_3Cl)^*$ of 1.4 × 10^{-11} s, presumably for the molecule in its triplet state. The lifetime is much shorter than those of the various excited states of the olefinic hydrocarbons and has been ascribed to enhanced intersystem crossing and phosphorescence as the result of the presence of an internal Cl atom.

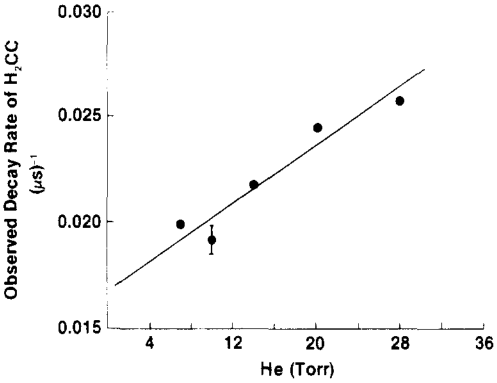

Figure 3. Observed decay rate of $H_2CC(^3B_2)$ as a function of helium pressure. Error bars are as noted in Figure 2.

Certainly the data in Figure 2 are suggestive that another excited state of C_2H_3Cl is accessed in the presence of He although the studies involving Hg photosensitization must populate the (π,π^*) triplet. We cannot with certainly identify the state from which dissociation via (4) occurs in the present work, but to allow for spin conservation it probably involves several rovibronic states in the (π,π^*) triplet manifold. If the production of $H_2CC(^3B_2)$ represents dissociation from that state, then a time derived from the intercept of Figure 2 representing the sum of the rate-limiting intersystem crossing process and vinylidene precursor lifetime equal to (3.7 ± 3.0) × 10^{-5} s is obtained.

Approximately half the vinyl chloride, 15 mtorr, is photodissociated during the flash and results in about 15 mtorr of both C_2H_2 and HCl; i.e., a mass balance was obtained. Though pressure variations of He affected the *rate* of product formation, the final concentration reached the same 15 mtorr, indicating that quenching of the particular triplet state of vinyl chloride either to a nondissociating state or to the ground state (X^1A_1) is relatively unimportant.

The single reported value for triplet vinylidene decay in He (k = (1.3 ± 0.3) × 10^{-14} cm^3 molecule^{-1} s^{-1}) was obtained at a single helium pressure where the triplet vinylidene was formed from the photolysis of acetylene.[22] The decay probably represents con-

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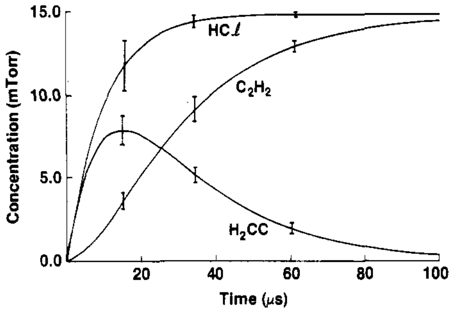

Figure 4. Calculated temporal profiles derived from the model. The indicated error bars were derived from using the upper and lower limits of the rate constants for the reactions used in the model. The species represented by each curve are the same as those in Figure 1.

version to acetylene. Data on the decay of $H_2CC(^3B_2)$ in helium derived in the present work is shown in Figure 3. The decay rate due to interaction of excited triplet vinylidene with He determined from the slope yields $k = (1.07 \pm 0.17) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The uncertainty represents one standard deviation from the linear least-squares fit of the data. The agreement between the reported values of the rate constants for quenching is very good particularly when considering that the mechanism of formation of the vinylidene is widely disparate in the two cases.

The intercept of Figure 3, 1.68×10^4 s^{-1}, clearly represents the interaction between $H_2CC(^3B_2)$ and both unphotolyzed C_2H_3Cl and the small amount of products. As noted above, half the vinyl chloride is photolyzed; hence the bimolecular rate constant for (5) of 3.5×10^{-11} cm^3 molecule^{-1} s^{-1} may be derived. Since there

$$H_2CC(^3B_2) + C_2H_3Cl \rightarrow H_2CC(^1A_1) + C_2H_3Cl \qquad (5)$$

is no loss of substrate, the rate constant for (5) probably represents, in large part, a quenching process. It may be expected that the quenching of $H_2CC(^3B_2)$ by vinyl chloride would be greater than the similar interaction of protonated triplet vinylidene with C_2H_4.[8] The difference, a factor of 2.5, is undoubtedly caused by the presence of an internal Cl atom which may promote intersystem crossing.

We have estimated that quenching of $H_2CC(^3B_2)$ results in $H_2CC(^1A_1)$ and hence C_2H_2. With the rate constants obtained in the present work we are able to model the system and account for all the product acetylene simply on the basis of the following scheme:

$$C_2H_3Cl + h\nu \rightarrow C_2H_3Cl^*$$

$$C_2H_3Cl^* + He \rightarrow H_2CC(^3B_2) + HCl(^1\Sigma^+)$$

$$C_2H_3Cl^* \rightarrow H_2CC(^3B_2) + HCl(^1\Sigma^+)$$

$$H_2CC(^3B_2) + He \rightarrow H_2CC(^1A_1) + He$$

$$H_2CC(^1A_1) \rightarrow C_2H_2$$

$$H_2CC(^3B_2) + C_2H_3Cl \rightarrow C_2H_2 + C_2H_3Cl$$

The data obtained from the model are shown in Figure 4. The results, which agree very well with the experimental data, support the interpretation that there is no other major source of acetylene in the system; hence the role of a 1,2 elimination of HCl is but a minor primary process in dissociation from the triplet vinyl chloride manifold.

In summary then, we have investigated the primary processes in the vinyl chloride photodissociation. The most probable pathway involves a crossing of the initially excited singlet substrate molecule to a long-lived triplet. The triplet C_2H_3Cl dissociates in a spin-allowed process into $H_2CC(^3B_2) + HCl(^1\Sigma^+)$. Rate constants for decay of the triplet vinyl chloride and the nature of the interaction between $H_2CC(^3B_2)$ and both He and C_2H_3Cl have been obtained. At present, the definite identity of the transient species whose absorption is at 137 nm has not been identified by high resolution spectroscopy; the evidence reported here and in previous papers from this laboratory strongly suggest that the carrier of the spectral feature is vinylidene. The quenching of vinylidene triplet by He ultimately yields C_2H_2 and the interaction with C_2H_3Cl similarly involves only quenching with no evidence for chemical reaction on the time scale of our experiments.

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Registry No. C_2H_3Cl, 75-01-4; H_2CC, 2143-69-3; HCl, 7647-01-0; C_2H_2, 74-86-2.

Ion Yields in Hydrocarbon Liquids Exposed to X-rays of 5–30-keV Energy

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Measurements of the yields of free ions, per unit absorbed dose, produced in three hydrocaron liquids due to X-ray exposure are reported. The yields increase with the applied field and increase with photon energy in the 5–30-keV range. The dependences on electric field and on the rate of energy loss, $d\mathcal{E}/dx$, are consistent with a track model. Electrons that would have escaped if ionizations were isolated do not escape because of recombination with adjacent ions in the track.

Introduction

The availability of synchrotron radiation has renewed interest in investigating the chemical, as well as biological, effects of X-rays. X-rays in the kiloelectronvolt range are found to be more effective per unit dose than γ rays in mediating radiation effects in cells.[1] Further, effects are enhanced around K- and L-absorption edges by tuning the X-ray energy to the energy of an element in a sample. Thus, the X-rays can be absorbed preferentially by one particular element. This selectivity contrasts with γ rays which interact more indiscriminately with a sample. In this study the physical interaction of X-rays with pure liquids is probed in a systematic way, measuring ionization yields as a function of X-ray energy. The results are quite different from similar studies with γ rays and suggest an increasing role of ion–electron recombination in the tracks in the case of X-rays. The results are also useful in interpreting EXAFS spectra obtained by the photoconductivity technique.[2]

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