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one may test directly various models for ICR signal damping (e.g., phase randomization vs frictional damping).[38]

The present results are quite general. The shape and position of the smooth curves in Figure 2 depend on ion trap cross-sectional shape (e.g., square or circular) and aspect ratio, but a given curve has the same shape for any size trap of a given shape, as will be described in detail elsewhere.[24]

Acknowledgment. We thank K.-P. Wanczek for private communication of his unpublished results on harmonic signals in a cylindrical ion trap. This work was supported by the NSF (CHE-8721498) and The Ohio State University.

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Photoionization (λ = 248 or 308 nm) of Triphenylmethyl Radical in Aqueous Solution. Formation of Triphenylmethyl Carbocation

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Received September 25, 1989

Short-lived carbocations have recently become accessible for study in nucleophilic environments, due to the development and application of fast-response radiation-chemical and photochemical methods. These involve four different types of cation production: (1) formation of a radical $R^\bullet$ followed by its one-electron oxidation with metal ions,[1,2] (2) photoheterolysis of RX,[3-10] (3) photoprotonation of a C=C double bond,[8,11] and (4) heterolysis of *radical* cations to give radicals and cations.[12,13] Concerning the radical oxidation method (1),[1,2] its obvious attractiveness lies in the fact that an enormously large number of radicals of the most diverse nature can be selectively produced by photochemical and, particularly, by radiation-chemical methods,[14] making the corresponding carbocations accessible after one-electron oxidation. However, an intrinsic drawback is that one-electron oxidation of the radical $R^\bullet$ to give the cation R^+ is a *bi*molecular process, the rate of which depends on the concentration of oxidant. In practice, the concentration of oxidant is often limited to ~1 mM, which means that, if the rate *constant* for oxidation of $R^\bullet$ is 10^9–10^{10} M^{-1} s^{-1} (i.e., diffusion control), the *rate* of R^+ formation is ~ 10^6–10^7 s^{-1}. Cations with lifetimes <100 ns can therefore not be studied with this method. A faster method of converting $R^\bullet$ into R^+ is therefore desirable, and it is in this respect that photoionization of $R^\bullet$ is an attractive possibility.

Aqueous solutions containing 0.4 mM triphenylacetic acid at pH 7–10, where the carboxyl group is ionized, were photolyzed with 20-ns pulses (10–100 mJ) of 248-nm light from a Lambda Physik EMG103MSC excimer laser, and the time-dependent optical and conductance changes were recorded with Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI $11/73^+$ computer, which also controlled the other functions of the instrument and performed on-line analysis of the experimental data.[15] As shown in Figure 1 (triangles), the photolysis leads to depletion of the parent (at 235 nm), to production of the triphenylmethyl radical (with its characteristic peak at 336 nm[16]), and to the hydrated electron, e_{aq}^- (which causes the broad band with λ(max) at 720 nm[17]). In agreement with this assignment, the 720-nm band (triangles) can be removed by admitting typical e_{aq}^- scavengers such as O_2, N_2O, or halogenated hydrocarbons such as CH_2Cl_2 or $HOCH_2CH_2Cl$ to the aqueous solutions (see Figure 1 (circles)). For $HOCH_2CH_2Cl$, the rate constant for reaction with e_{aq}^- was determined as 4.2×10^8 M^{-1} s^{-1},[18] in agreement with literature values.[19]

The yield of $Ph_3C^\bullet$ and of e_{aq}^- increases with the *square* of the incident laser power, varied in the range 0–40 mJ/pulse, which means that the production of $Ph_3C^\bullet$ and e_{aq}^- from $Ph_3CCO_2^-$ requires *two* photons (eq 1a). $Ph_3C^\bullet$ could be generated biphotonically also from Ph_3CH (eq 1b) or by reaction of Ph_3CH or $Ph_3CCO_2^-$ with photochemically (eq 2a) or radiation-chemically (eq 2b) produced $SO_4^{\bullet -}$, eq 3, indicating that the common precursor is the radical cation. Rapid decarboxylation or deprotonation of one-electron-oxidized phenylacetic acid and toluene derivatives is well documented.[20]

$$Ph_3CCO_2^- \xrightarrow[248\ \mathrm{nm}]{h\nu} Ph_3CCO_2^{-*} \xrightarrow[248\ \mathrm{nm}]{h\nu} Ph_3C^\bullet + CO_2 + e_{aq}^- \tag{1a}$$

$$Ph_3CH \xrightarrow[248\ \mathrm{nm}]{h\nu} Ph_3CH^* \xrightarrow[248\ \mathrm{nm}]{h\nu} Ph_3C^\bullet + H^+ + e_{aq}^- \tag{1b}$$

$$S_2O_8^{2-} \xrightarrow[248\ \mathrm{nm}]{\overset{a}{h\nu}} 2SO_4^{\bullet -};\ S_2O_8^{2-} + e_{aq}^- \xrightarrow{b} SO_4^{2-} + SO_4^{\bullet -} \tag{2}$$

$$Ph_3CR \xrightarrow[\text{or } 2h\nu/-e^-]{SO_4^{\bullet -}/-SO_4^{2-}} Ph_3CR^{\bullet +} \rightarrow Ph_3C^\bullet + R^+;\ R = H,\ CO_2^- \tag{3}$$

As seen in inset b of Figure 1, $Ph_3C^\bullet$ produced by biphotonic ionization of $Ph_3CCO_2^-$ is quite long-lived (it decays bimolecularly on a longer time scale). After a few microseconds (typically 1–8 μs), the solution was subjected to a second 20-ns laser pulse[21] either

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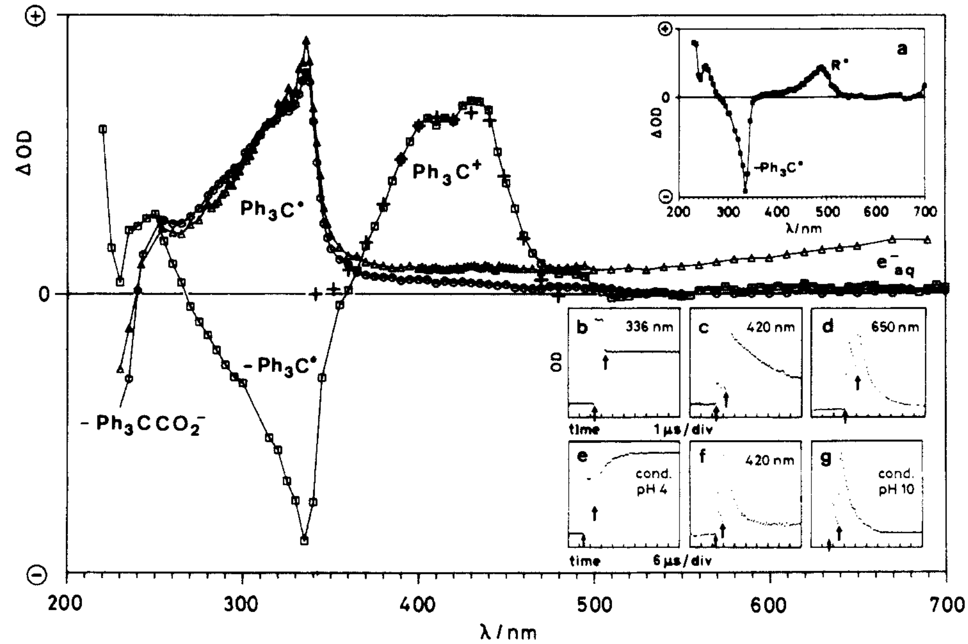

Figure 1. Absorption spectra of transients produced by photolysis of a 0.4 mM solution of triphenylacetic acid at pH 7.5, deoxygenated with Ar. The arrows indicate the pulse positions. Triangles: ΔOD recorded 560 ns after the *first* pulse (with 248-nm light, 20-ns duration). Circles: 0.12 M $HOCH_2CH_2Cl$ added to scavenge e_{aq}^-. Squares: spectrum recorded 320 ns after the *second* pulse (308-nm light, 20 ns), delayed 1 µs from the first. Crosses: absorption spectrum of Ph_3C^+ in 60% H_2SO_4 obtained by dissolving 0.04 mM Ph_3COH. Inset a shows the spectrum recorded 530 ns after the *second* pulse in the presence of 1 mM NaN_3, added to scavenge Ph_3C^+. Insets b–d show (b) the depletion of Ph_3C^+ at 336 nm and (c) the formation of Ph_3C^+ at 420 nm and (d) of e_{aq}^- at 650 nm. The remaining insets show the decay of Ph_3C^+, by reaction with H_2O: solution e contains 0.3 mM Ph_3CH in H_2O–CH_3CN, 2:1 (v/v), at pH 4, and f and g are 0.4 mM $Ph_3CCO_2^-$ in H_2O at pH 10.

with 308 nm (10–40 mJ) or with 248 nm (20–100 mJ) from a Lambda Physik EMG 150 E laser. The delay between the first pulse (the "synthesis pulse"[22]) and the second (the "photolysis pulse"[22]) could be varied from 10 ns to the millisecond range by a computer-controlled delay generator.

From inset b it is evident that the second pulse (308 nm) leads to a depletion of $Ph_3C^•$. By this reaction is produced a transient that absorbs at 420 nm (inset c) and one at 650 nm (inset d). The spectrum of the latter (not shown; it is broad with a peak at ≈720 nm) is assigned to e_{aq}^-, essentially on the basis of its reactivity[23] with e_{aq}^- scavengers. The formation of e_{aq}^- resulting from the depletion of $Ph_3C^•$ by the second pulse shows that this process is photoionization. The yield of e_{aq}^- (and of Ph_3C^+, see below) was linearly dependent on the photon flux at 308 nm, suggesting that the photoionization is a monophotonic process. The thermodynamics of this reaction are in line with this conclusion. The IP of $Ph_3C^•$ is 7.26 eV, a 308-nm photon provides 4.03 eV, and the missing 3.2 eV can be supplied by the hydration energy of e_{aq}^- and a cation, which amounts to 2.5–3.5 eV.[24]

In Figure 1 (squares) is shown the absorption spectrum of the transient absorbing in the 400–450-nm region (in a solution containing $HOCH_2CH_2Cl$ to scavenge e_{aq}^-), and the spectrum is compared with that (crosses) of Ph_3C^+ in 60% H_2SO_4. The spectra are obviously very similar[25] (also with that[7] of photoheterolytically produced Ph_3C^+ in water–acetonitrile mixtures), and the transient produced from $Ph_3C^•$ is thus identified as Ph_3C^+ (see eq 4). From a quantitative comparison of the OD changes due to *depletion* of $Ph_3C^•$ (ϵ(334 nm) = 3.6×10^4 M^{-1} cm^{-1})[16] with those for *formation* of Ph_3C^+ (ϵ(428 nm) = 3.9×10^4 M^{-1} cm^{-1}),[7] it is evident that the efficiency of the photochemical conversion of $Ph_3C^•$ into Ph_3C^+ is 75–85%.

$$Ph_3C^• \xrightarrow[248 \text{ or } 308 \text{ nm}]{h\nu} Ph_3C^+ + e^- \quad (4)$$

$$Ph_3C^+ + H_2O \rightarrow Ph_3COH + H^+ \quad (5)$$

Ph_3C^+ decays in the aqueous solution exponentially, due to its reaction with water, eq 5, with $k = 1.7 \times 10^5$ s^{-1} at ≈25 °C, a value very similar to that (1.5×10^5 s^{-1}) measured previously[7] in water–acetonitrile mixtures. This decay is seen in insets c and f, and it is also demonstrated (inset e) that this process is accompanied by a conductance *in*crease in acid solution (due to production of H^+, eq 5) and by a conductance *de*crease (inset g) in basic solution (due to removal of OH^- by the H^+ generated in eq 5). The pH-dependent inversion of the polarity of the conductance signal is unequivocal evidence for the cationic nature of the species responsible for the conductance changes. Further support for its identification as Ph_3C^+ is its reactivity with the nucleophile N_3^-. $k(Ph_3C^+ + N_3^-)$ was measured (by the decay at 420 nm) to be 4.2×10^9 M^{-1} s^{-1}, practically the same as that (4.1×10^9) determined[7] in water–acetonitrile, 2:1. In inset a is shown the spectrum, produced from $Ph_3C^•$ by the 308-nm pulse, that remains after quantitative scavenging of Ph_3C^+ by N_3^-. The spectrum is assigned in terms of 4a,4b-dihydro-9-phenylfluorenyl radical, cf. ref 25.

The trityl cation, Ph_3C^+, can also be produced from $Ph_3CCO_2^-$ or Ph_3CH with *one* pulse of 248-nm light (see, e.g., the prepulse trace in inset f).[28] Since this method requires *three* photons, the yield of Ph_3C^+ increases very strongly with increasing photon density. For practical purposes, a pulse power ≥100 mJ is required

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(25) Close inspection of Figure 1 (squares) shows that there is a shoulder at ≈490 nm which does *not* belong to Ph_3C^+. This signal has been seen before[26] on photolysis of $Ph_3C^•$ and tentatively assigned[22c,26,27] to the cyclization product, 4a,4b-dihydro-9-phenylfluorenyl radical (inset a shows the "clean" spectrum $R^•$, after removal of Ph_3C^+, see text).

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to obtain noticeable concentrations of Ph_3C^+.

Conclusion. It has been demonstrated that, in a polar solvent such as water, a neutral radical can be photoionized to give the corresponding carbocation. In most cases, the rate of this conversion is likely to be limited only by the length of the ionizing light pulse, in which case it should be possible to produce and study ultrareactive cations with lifetimes, e.g., in the picosecond domain.

Acknowledgment. J.L.F. thanks the Deutscher Akademischer Ausstauschdienst (DAAD) for a stipend.

Proton-Detected 2D Heteronuclear Shift Correlation via Multiple-Quantum Coherences of the Type I_2S

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Received August 23, 1989

NMR spectroscopy of high molecular weight compounds suffers from overlap problems giving rise to severe difficulties in spectral assignments. 3D NMR measurements[1] are helpful in simplifying spectral patterns but require an enormous amount of computational effort. Alternatively, filtering methods offer the possibility of selectively extracting spectral information from isotope-labeled compounds.[2] In order to provide maximum sensitivity, these so-called editing techniques very often are based on the application of polarization transfer protocols in conjunction with proton detection. We are reporting here on such a pulse sequence, which allows one to exclusively detect heteronuclear spin systems of the type I_2S, I and S representing protons and heteronuclei, respectively. This type of selection is extremely useful in discriminating asparagine and glutamine side-chain amide protons from those located in the peptide backbone, as will be shown for uniformly ^{15}N-labeled RNase T_1. Although the NH_2 resonances could be identified on the basis of the 0.6 ppm NHD isotope effect, they are likely to be covered by other signals, especially in spectra of larger proteins.

In the following, the basic ideas leading to the design of this particular 2D NMR experiment are summarized. The large heteronuclear one-bond coupling of approximately 90 Hz allows fast excitation of proton–heteronucleus multiple-quantum coherences, including the nitrogen nucleus as a relay site. Usually, the homonuclear coupling constants are 1 order of magnitude smaller and require much longer preparation periods. The selection between different spin topologies depends on these correlations. Consequently, resonances from side-chain amides can be distinguished from those of backbone amides.

A modified DEPT sequence has proven to be suitable for the stepwise preparation of triple-quantum coherences.[3,4] From symmetry considerations, we concluded that a time-reversed DEPT-type sequence would allow the conversion of the triple-quantum coherences into detectable single-quantum terms. This leads to the pulse sequence depicted in Figure 1. In a back-to-back manner, both DEPT pulse clusters flank the evolution period during which chemical-shift labeling of protons with the heteronuclei precession frequencies takes place. Proton chemical-shift contributions were removed by employing selective inversion of proton populations in the middle of the evolution period. Thus, triple-quantum and single-quantum coherences were exchanged, leaving the heteronuclear precession unaffected.

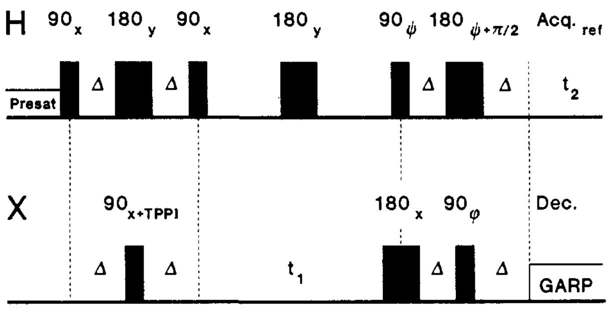

Figure 1. Pulse scheme for heteronuclear shift correlation via I_2S three-quantum coherences. The delay Δ should match $1/(2J_{NH})$. The phases are cycled as follows: $\varphi = x, -x$; $\psi = x, x, -x, -x, y, y, -y, -y$; ref $= x, -x, -x, x, -y, y, y, -y$.

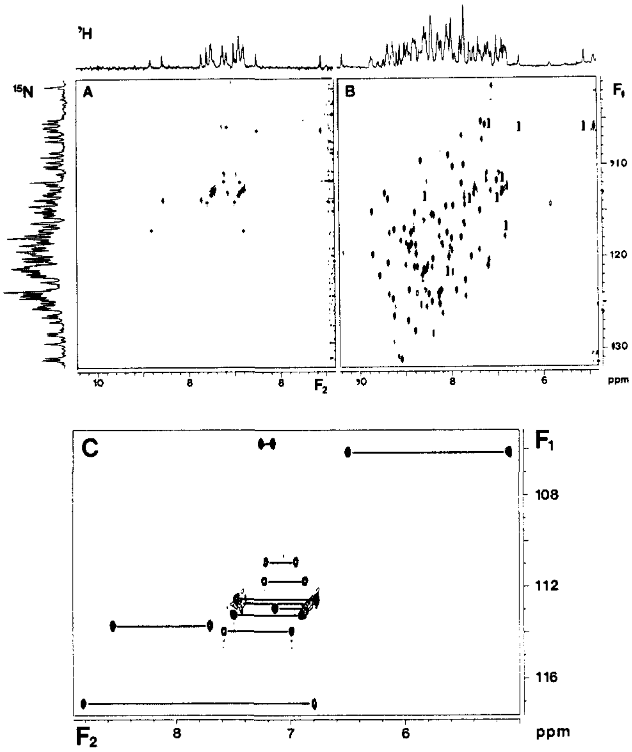

Figure 2. Selective heteronuclear shift correlation spectra for terminal amide groups in side chains of asparagine and glutamine residues (A) and for all amides (B) in uniformly ^{15}N-labeled RNase T_1; the $^{15}NH_2$ correlations are indicated in the expansion (C). Both spectra are represented in a pure absorption mode. Prior to FT, the 256 increments of 2K data points were zero-filled once in t_2 and twice in t_1. The total spectral widths covered 2000 Hz in F_1 and 6250 Hz in F_2. In order to account for relaxation effects, the delay Δ was set to 5.0 ms, which is slightly shorter than $1/(2J_{NH})$.

Since proton chemical shifts are completely refocused, the experiment reveals pure absorptive signals in the F_2 dimension. The signals in F_1, owing to delayed t_1 acquisition, will be phase-modulated unless an additional refocusing pulse in the nitrogen channel is applied. A refocusing pulse coincident with one of the two proton mixing pulses restores the initial phase relations, thus allowing the nitrogen signals to be represented in a pure absorption mode. Since control of the signal phase is kept separate for each species of nucleus, the TPPI method[5] is applicable for phase-sensitive detection of heteronuclear shifts.

The experiment was performed on a Bruker AM-500 spectrometer equipped with a 5 mm reverse broad-band probe tuned to a 500.13 MHz proton frequency. A sample of fully ^{15}N-labeled RNase T_1 was obtained from *Escherichia coli* by recombinant techniques.[6,7] The isoenzyme contains nine asparagine and two

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