# Unimolecular Dissociation of Radical Cations of Monoalkyl Acetals

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Williams and his co-workers have recently demonstrated that the odd electron in radical cations of acetals produced in $\gamma$-irradiated Freon solutions at 77 K is highly delocalized between the two oxygen atoms via the bridging methylene group.[1a] In this communication we report that the radical cations of monoalkyl acetals, $R'OCHROR''^{+}$, suffer a unimolecular dissociation as in eq 1. The alkyl radical can be identified unmistakably by its ESR

$$R'OCHROR''^{+} \rightarrow R'OCHOR''^{+} + \cdot R \qquad (1)$$

signal and the accompanying carbonium ion by its strong absorption in the UV region. The precursor radical cations can only be stabilized at temperatures near 4.2 K under darkness for some of the acetals.

The monoalkyl acetals studied in this work include 2-methyl-1,3-dioxacyclopentane, 2-methyl-1,3-dioxacyclohexane, 3-methyl-2,4-dioxapentane, 2,4,6-trimethyl-1,3,5-trioxacyclohexane and their ethyl analogoues. These were dissolved in $CCl_3F$ and irradiated at 4.2 and 77 K. The experimental procedure for the ESR and optical absorption spectra is described in our previous paper.[2] When the samples were irradiated and measured at 77 K, all the samples exhibited ESR spectra almost solely due to the methyl or ethyl radical in accordance with eq 1. The samples also exhibited a strong UV absorption band with the absorption maximum of about 310 nm and $\epsilon_{max} \simeq 5.5 \pm 1.0) \times 10^4$ L mol$^{-1}$ cm$^{-1}$ (cf. Figure 1D). As will be discussed below, this absorption is attributed to the carbonium ion produced in eq 1.

The observation of the unimolecular decomposition in the condensed phase implies that the ionization potential of the acetal radical $IP(R'O\dot{C}HOR'') \lesssim 7$ eV on the basis of the arithmetic of the ionization potential of the parent acetals ($IP(R'OCHROR'') \simeq 10.5$ eV[3]) minus the dissociation energy of the alkyl group ($DE(R'O\dot{C}HOR'' + \dot{R}) \simeq 3.5$ eV). It is noted that the ionization potential of the acetal radical is lower as much as by $\gtrsim 2$ eV than the standard ionization potential of the unsubstituted methyl radical of about 9.0 eV.

The out-of-plane lone-pair orbitals on the two oxygen atoms and the vacant $\pi$ orbital on the bridging methine in the carbonium ion form a favorable molecular orbital for the four $\pi$ electrons. A semiempirical MO calculation of CNDO/S type indicates that the first electronic transition of the carbonium ion is of the character of intramolecular charge transfer from the two oxygens to the central methine carbon. Such a situation is different from the standard carbonium ion, which does not absorb at wavelengths longer than 210 nm.[5]

In order to see whether the precursor radical cation in eq 1 can be detected if the temperature of irradiation and measurement is lowered, we carried out experiments at the liquid helium temperature. The ESR spectrum in Figure 1A was obtained for 2-methyl-1,3-dioxacyclopentane in $CCl_3F$ (1:100 mole ratio) irradiated and measured at 4.2 K. Besides the signal due to color centers and the partial revelation of the methyl radical a broad doublet with a separation of about 100 G is seen. The doublet was very sensitively bleached with room light, and the methyl radical concentration increased. Similarly, when the sample at 4.2 K was transferred to a liquid nitrogen bath under darkness, the doublet disappeared completely, and the methyl signal increased remarkably as shown in Figure 1B. The result suggests that the precursor radical cation is metastable at 4.2 K but decomposes very easily according to eq 1 both thermally and photolytically.

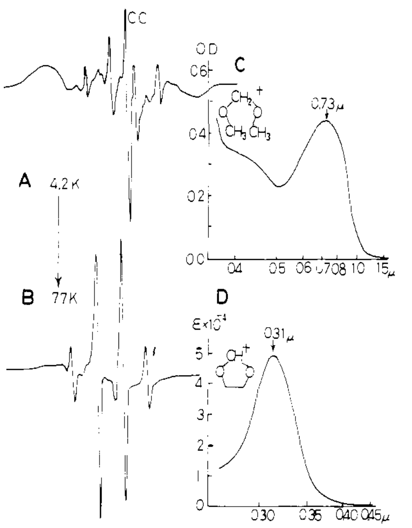

Figure 1. (A) ESR spectrum of 2-methyl-1,3-dioxacyclopentane in $CCl_3F$ (1:100 mole ratio) irradiated and measured at 4.2 K under darkness. (B) Same as above measured at 77 K. (C) The optical spectrum of 2,4-dioxapentane in $CCl_3F$ (1:100 mole ratio) irradiated and measured at 77 K. The absorption maximum is attributed to the charge resonance band of the radical cation involving the molecular orbitals $n_1 \pm n_2$.[1b,3] The broad bump at about 450 nm is also attributed to the radical cation in reference to a relevant photoelectron spectrum.[3] (D) The optical spectrum corresponding to 1B.

Although the optical measurement at 4.2 K was not carried out, we conjecture that the parent radical cation absorbs in the visible to near IR region by analogy with the radical cations of unsubstituted acetals.[1b] The latter exhibit an absorption in the same wavelength region as shown representatively for the case of 2,4-dioxapentane in $CCl_3F$ irradiated and measured at 77 K (cf. Figure 1C). The corresponding sample exhibits an ESR spectrum of a triple–triplet, which has been attributed to the radical cation where the odd electron resides in the molecular orbital consisted mainly of the in-phase combination of the lone pair orbitals, $n_1$ and $n_2$, of the two oxygens.[1a,b] The visible to near IR absorption is associated with the electron transfer from the molecular orbital $n_1 - n_2$ to $n_1 + n_2$.[1b] In passing, we point out that the assignment of the previous photoelectron spectroscopic study showing that $n_1 - n_2$ is HOMO and $n_1 + n_2$ is next-to-HOMO is inconsistent with the ESR studies.[1a,b] The relative instability of the radical cations of monoalkyl acetals may be due to the smaller dissociation energy DE than that of the unsubstituted acetals.

As for the ethyl-substituted acetals all the samples studied yielded a clear spectrum due to the ethyl radical when irradiated and measured at 77 K. However, the samples irradiated and measured at 4.2 K gave complicated spectra that were not affected upon photobleaching as long as the sample were kept at 4.2 K. The complicated spectra changed irreversibly to the normal spectrum of the ethyl radical[6] when the samples were warmed from 4.2 to 77 K. We conjecture that the radical cations of the ethyl acetals are subject to bond breakage already at 4.2 K, but due to the constriction at the low temperature the ethyl radical interacts with the counterpart carbonium ion to such an extent as to yield the observed complicated spectrum. The warming causes the separation of the interacting pair and gives the normal spectrum of the ethyl radical.

In conclusion, we have demonstrated a noval example of a very

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(7) **Note Added in Proof**: Recently we have noted that the radical cations of acetals have also been studied by Symons et al. [Symons, M. C. R.; Wren, B. W. *J. Chem. Soc., Chem. Commun. No. 15*, 817, 1082].

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subtle unimolecular decomposition of radical cations at low temperatures.

**Registry No.** 2-Methyl-1,3-dioxacyclopentane, 497-26-7; 2-methyl-1,3-dioxacyclohexane, 626-68-6; 3-methyl-2,4-dioxapentane, 534-15-6; 2,4,6-trimethyl-1,3,5-trioxacyclohexane, 123-63-7; 2-ethyl-1,3-dioxacyclopentane, 2568-96-9; 2-ethyl-1,3-dioxacyclohexane, 5702-29-4; 3-ethyl-2,4-dioxapentane, 4744-10-9; 2,4,6-triethyl-1,3,5-trioxacyclohexane, 2396-42-1; dimethoxymethyl radical cation, 81027-72-7; 4,5-dihydro-1,3-dioxol-1-ium, 6680-54-2.

## Analysis of Hydrocarbon Chain Conformation Using Double Quantum Coherence $^{13}$C NMR

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An understanding of the conformational and dynamic properties of hydrocarbon chains is of interest in connection with a wide variety of problems, including the structure and function of biological membranes[1] and surfactants.[2] A full understanding of these systems requires an integrated model containing both conformational and dynamic parameters. Carbon-13 spin lattice relaxation rates have found particular application in describing the dynamics of gauche/trans isomerization.[3-5] Temperature-dependent $^{13}$C chemical shifts have been suggested to reflect the gauche/trans conformational equilibrium,[6-8] but recent attempts to develop this parameter as a quantitative tool have indicated significant complications.[8] The chemical shift difference between a gauche and a trans conformation may depend strongly on the particular carbon position, in contrast to previous assumptions,[8] and in some cases of branched alkanes the model appears to break down completely. Scalar coupling constants have long been used as a basis for conformational analysis;[9] however, applications are limited by the abundances of various nuclear species and by the complexity of the spectra. The recent development of a double quantum coherence method for the observation of $^{13}$C–$^{13}$C scalar coupling constants without the need for isotopic labeling provides an alternative approach to the hydrocarbon chain conformation problem.[10] The method is particularly suitable for this application since one-, two-, and three-bond carbon–carbon coupling constant values in hydrocarbons are typically of significantly different magnitudes,[11] and observation of coupling constants of selected magnitude may be enhanced by the appropriate choice of pulse intervals.[10] Consequently, $^3J_{CC}$ values, which are dependent on the subtended dihedral angle, can be selectively observed.

In order to evaluate the potential of this approach, we have carried out studies on a 90% octanol–10% benzene-$d_6$ solution, with the latter serving for the deuterium lock. A representative $^{13}$C double quantum coherence spectrum of the region containing the octanol C-7 resonances with pulse intervals chosen to optimize couplings with magnitude close to 4.0 Hz is illustrated in Figure 1, and the corresponding coupling data are tabulated in Table I. For carbons near the ends of the chain there is only a single vicinal coupling interaction so that the observed coupling constant can be unequivocally associated with a particular bond conformation. Alternatively, for carbons 4 and 5 the observed coupling constants correspond to a superposition of the $^3J_{41}$ and $^3J_{47}$ values in the first case, and the $^3J_{52}$ and $^3J_{58}$ values in the second. Thus, the observed C-4 doublet should exhibit a splitting that is approximately the average of the values observed for C-1 and C-7, as is observed (Table I). For a sufficiently short chain as in the present example, it is not necessary to utilize the data obtained for the unresolved carbon splittings corresponding to C-4 and C-5.

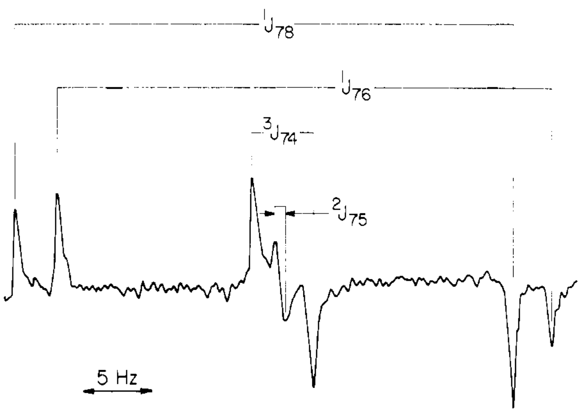

**Figure 1.** Double quantum coherence spectrum of the C-7 resonances of *n*-octanol in a 90% *n*-octanol–10% benzene-$d_6$ solution, obtained as described by Bax et al.[10] $(90^\circ_x\text{-}\tau\text{-}180^\circ_y\text{-}\tau\text{-}90^\circ_x\text{-}\Delta\text{-}90^\circ(\Phi))$. Spectra were obtained on a JEOL FX 90Q NMR spectrometer in 10-mm sample tubes by using 32K time domain data points and a 1500-Hz spectral width, to provide a resolution of 0.09 Hz. This spectrum was obtained by using a $\tau$ value of 63 ms (optimizing for 4-Hz C–C coupling), a repetition rate of 15 s, and a total of 4000 scans (total accumulation time 17 h).

Table I. Vicinal Carbon–Carbon Coupling Constants in *n*-Octanol as a Function of Temperature[a]

| carbon | $^3J_{CC}$-(30°) | $^3J_{CC}$-(65°) | $^3J_{CC}$-(100°) | $^3J_{CC}$-(150°) |
|---|---|---|---|---|
| C-1 | 4.30 | 4.21 | 4.12 | 4.04 |
| C-2 | 3.76 | 3.57 | 3.67 | 3.58 |
| C-3 | 3.94 | 3.85 | 3.75 | 3.67 |
| C-4 | 4.12 | 3.93 | 3.94 | 3.85 |
| C-5 | 4.03 | 3.75 | 3.66 | 3.67 |
| C-6 | 3.94 | 3.85 | 3.76 | 3.66 |
| C-7 | 4.03 | 3.85 | 3.75 | 3.66 |
| C-8 | 4.03 | 4.03 | 3.84 | 3.67 |

[a] Values measured with a resolution of 0.09 Hz.

Interpretation of the coupling data in terms of chain conformation is based on a model in which the hydrocarbon chain is described as an equilibrium mixture of rapidly interconverting trans and gauche conformers about each bond. Two approaches have been utilized to estimate the pure trans and gauche coupling constants. In the first, a theoretical self-consistent field, finite perturbation theory treatment at the INDO level of approximation was used.[12] In previous studies with $^{13}$C-enriched amino acids, we have found that these calculations give qualitatively reasonable predictions for $^1J_{CC}$ and $^3J_{CC}$ but relatively poor agreement for $^2J_{CC}$.[13] For reasons of time and convenience, calculations were carried out on *n*-heptanol, and the results for trans and gauche coupling constants along the chain are summarized in Figure 2a. With the exception of $^3J_{14}$, for which a significant substituent effect

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