latter is a relaxation process that occurs in parallel with the EE; both are due to electron-hole recombination. Strong evidence for the occurrence of the gaseous breakdown is the RE and the intense component of phE occurring during fracture.

One final result that was not reported above that should be noted is that, after fracture under vacuum, the Wint-o-green Lifesavers tasted rather bland. Although we have not performed the control experiment, we are confident that fracture had nothing to do with the change in flavor. One must ask, in addition, what influence FE might have on the physiological experience of eating

Lifesavers.

Acknowledgment. We thank E. E. Donaldson and A. Jahan-Latibari for their contributions to this research and helpful discussions. This work was supported by the Office of Naval Research, Contract N0014-80-C-0213, the National Science Foundation, Grant DMR 8210406, Sandia National Laboratories, NASA—Ames Research Center, and the M. J. Murdock Charitable Trust.

Registry No. Sucrose, 57-50-1.

An ESR Investigation of Ester π -Cation Radicals in a Freon Matrix at Low Temperatures: Evidence for Unusual Barriers to Methyl Group Rotation and Intramolecular Bonding

Michael D. Sevilla,* David Becker, Cynthia L. Sevilla, and Steven Swarts

Department of Chemistry, Oakland University, Rochester, Michigan 48063 (Received: August 11, 1983)

 γ -Irradiation of dilute solutions of a number of esters in CFCl₃ at 77 K is shown by ESR spectroscopy to produce the π -cation radicals of these molecules. The π -cations formed are those of the methyl and ethyl formates, acetates, and propionates. Larger esters containing propyl and butyl side chains are suggested to be unstable toward deprotonation at 77 K. Synthesis of deuterium-labeled compounds was employed to assign proton hyperfine couplings to specific sites in the π -cation radicals. The π -cations of the ethyl esters show unusually large couplings to the terminal methyl groups. In addition, large barriers to methyl group rotation are found for both the methyl and ethyl ester cation radicals. The large barriers suggest intramolecular bonding between the alkyl group and the carbonyl oxygen in the ester functional group. Such a hypothesis is supported by the finding of a torsional motion in the terminal methyl group of ethyl formate *π*-cation which has a ca. 1.7 kcal/mol activation energy barrier. We suggest that a new intramolecular π^* -bond is responsible for the formation of cyclic rings in the methyl- and ethyl-substituted ester cation radicals.

Introduction

Since the recent development of techniques to produce isolated cation radicals of small organic molecules in γ -irradiated Freon matrices at low temperatures, a considerable interest has developed in these species.¹⁻⁶ It is now becoming evident that some of these cation radicals possess unique properties which are not observed in neutral free radicals or anion radicals. As an example, strong electron-deficient bonding to the Freon matrix has been observed in methyl formate radical cation,⁷ and weak superhyperfine interactions to the matrix have been characterized in acetaldehyde radical cation.⁸ In addition, unusually large barriers to methyl group rotations have been observed in methyl formate π -cation⁷ and alkane π -cations.^{1,6,9,10} In this paper we wish to report (1) further experimental confirmation of the existence of large barriers to methyl group rotations in ester radical cations, which we suggest is due to internal electron-deficient bonding, and (2) examples

of unusually large proton hyperfine couplings, which we ascribe to efficient hyperconjugation and/or the internal bonding itself.

An interesting chemistry is developing around the small organic cations formed by irradiation in Freon matrices at low temperatures. It is becoming apparent that electron-deficient bonding of the solute cations to solvent⁷ and, as shown in this work, internally to themselves is a dominant feature of this chemistry. Using the concepts of orbital interaction developed most recently by Salem,^{11,12} we can describe, qualitatively, the electron-deficient bonding by postulating the formation of new bonding and antibonding MOs through the interaction of orbitals of proper symmetry and spatial orientation and net stabilization through loss of an electron (for cationic species) from an antibonding orbital.

In this work, using the concept of group orbitals,¹² we describe electron-deficient intramolecular π^* -bonding. It seems likely that an understanding of the intramolecular and intermolecular bonding of these cationic species and of their chemistry and electronic structure will provide insight into analogous intermediates in oxidative reaction mechanisms.

Experimental Section

Samples were prepared from commercially available compounds and checked for purity by gas-liquid chromatography. Esters deuterated at various positions were found to be essential to the interpretation of ESR spectra of the π -cation radicals and were prepared in our lab using standard preparative methods. Gas-

⁽¹⁾ Wang, J. T.; Williams, F. J. Phys. Chem. 1980, 84, 3156.

⁽²⁾ Snow, L. D.; Wang, J. T.; Williams, F. J. Am. Chem. Soc. 1982, 104, 2062.

 ⁽³⁾ Shida, T.; Kato, T. Chem. Phys. Lett. 1979, 68, 106.
 (4) Shida, T.; Egawa, Y.; Kubodera, H. J. Chem. Phys. 1980, 73, 5963. (5) Kubodera, H.; Shida, T.; Shimokoshi, K. J. Phys. Chem. 1981, 85, 2583.

⁽⁶⁾ Symons, M. C. R. "Electron Spin Resonance Spectroscopy"; Royal Society of Chemistry: 1981; Annual Reports, Vol. 78, Section C, p 151. (7) Becker, D.; Plante, K.; Sevilla, M. D. J. Phys. Chem. 1983, 87, 1648.

⁽⁸⁾ Snow, L. D.; Williams, F. Chem. Phys. Lett., in press

⁽⁹⁾ Iwasaki, M.; Toriyama, K.; Nunome, K. J. Am. Chem. Soc. 1981, 103, 3591.

⁽¹⁰⁾ Toriyama, K.; Nunome, K.; Iwasaki, M. J. Chem. Phys. 1982, 77, 5891.

⁽¹¹⁾ Salem, L. "Electrons In Chemical Reactions"; Interscience: New York, 1982.

⁽¹²⁾ Jorgensen, W. L.; Salem, L. "The Organic Chemists Book of Orbitals"; Academic Press: New York, 1973.

TABLE I:	Proton and Deuteron	Hyperfine Coupling	Constants of π -Cations i	in Annealed CFCl ₃ Solution (All	Values Are Reported in gauss) ^a
----------	---------------------	--------------------	-------------------------------	---	--

	a _{acyl}	$a_{\beta}^{\mathbf{H}(\mathbf{D})}$	aH	<i>Т</i> , К
methyl formate HCO ₂ CH ₃ ^b DCO ₂ CH ₃	5.6	23 (2 H), 4 (1 H) 23 (2 H), 4.0 (1 H)		145 145
methyl acetate CH ₃ CO ₂ CH ₃ CH ₃ CO ₂ CD ₃	5.2 (3 H) 5.2 (3 H)	21.8 (2 H) 3.5 (2 D)		139 77-145 ^c
methyl propionate CH ₃ CH ₂ CO ₂ CH ₃ CH ₃ CH ₂ CO ₂ CD ₃	7 (1 H)	25 (2 H) singlet		125
ethyl formate HCO ₂ CH ₂ CH ₃ DCO ₂ CH ₂ CH ₃ DCO ₂ CH ₂ CD ₃	3-4	22.2 (2 H) 22.7 (2 H) 22.5 (2 H)	10.8 (2 H) ^d 9.8 (2 H) ^d	141 141 143
ethyl acetate CH ₃ CO ₂ CH ₂ CH ₃ CD ₃ CO ₂ CH ₂ CH ₃		22 (1 H), 31 (1 H) 22 (1 H), 31 (1 H)	8 (1 H), 17 (1 H) 8 (1 H), 17 (1 H)	123 123
ethyl propionate CH ₃ CH ₂ CO ₂ CH ₂ CH ₃		23.0 (2 H)	$10.9 (2 \text{ H})^d$	138

^a The g values for all of the π -cations were near 2.0025. ^b Reference 7. ^c No temperature dependence was observed for these splittings over this temperature range. ^d This splitting is the result of motional averaging of inequivalent γ -proton couplings (see text).

liquid chromatography was used for separation and purification of the deuterated esters, and NMR spectra were employed to confirm deuterium substitution when any doubt was present. Samples of esters in CFCl₃ were irradiated in Spectrosil quartz tubes at 77 K for doses of 0.2 Mrd. Samples were investigated at a variety of concentrations as the concentration of solute was found to be an important factor. An initial ESR spectrum was taken within 1-4 h after irradiation. A Varian Century ESR spectrometer with an E-4531 dual cavity was employed. Hyperfine splittings and g values were measured vs. Fremy's salt with A_N = 13.09 G and g = 2.0056.

Results

In this section we report the results of the γ -irradiation of dilute (0.2-1 mol %) samples of various esters in CFCl₃ at 77 K. For methyl acetate, ethyl formate, ethyl acetate, methyl propionate, and ethyl propionate the spectra found were consistent with formation of π -cation radicals. The π -cations of the ethyl esters showed a temperature dependence in their spectra as the samples were warmed. The temperature dependence is shown to be due to a conformational interconversion and is analyzed in detail for the ethyl formate cation. The results reported in Table I are for the high-temperature region for the ethyl esters at which the interconversion is rapid. Selective deuteration of specific sites in the ester molecules was employed in order to assign couplings to sites on the ester cation structures. In all of the esters which produce π -cations, hyperfine coupling to the alcohol alkyl group rather than to the acid alkyl group predominates. This pattern of coupling is consistent with the π -nature of the radicals.

Methyl Acetate Cation. The ESR spectrum of methyl acetate (1%) in CFCl₃ is shown in Figure 1A. The sample was irradiated at 77 K and the best resolution found at 139 K. The spectra for this radical show no evidence of the σ^* -matrix complex found previously for methyl formate.⁷ The ionization energy of the CFCl₃ matrix is 11.78 eV, that of methyl acetate 10.27 eV, and that of methyl formate 10.815 eV.¹³ Since the formation of the σ^* -matrix complex depends on the proximity of the ionization energies of the two interacting structures,^{7,14,15} the 0.6-eV lower ionization energy of methyl acetate relative to that of methyl formate greatly reduces the likelihood of complex formation of methyl acetate with CFCl₃.

The spectrum in Figure 1A consists of a 22.5-G triplet further split by a more poorly resolved 5.2-G quartet. In view of our results found for the isolated methyl formate π -cation (Table I),



Figure 1. (A) First-derivative ESR spectrum of the methyl acetate π -cation found at 139 K after γ -irradiation of a 1% (mol/mol) solution in CFCl₃ at 77 K and annealing to 139 K. The spectrum at 77 K is essentially the same, but does not show the small 5.2-G splitting. (B) Experimental spectrum (top) of the π -cation of deuterated methyl acetate in CFCl₃ (1% mol/mol), irradiated and recorded at 77 K. Warming to 139 K did not significantly improve the resolution. The lower tracing is a computer simulation assuming isotropic couplings of 5.2 G (3 H) and 3.5 G (2 D). The three reference marks in the experimental spectrum are separated by 13.09 G; the central mark is at g = 2.0056. Note that the calibration of the horizontal axes are different for the two experimental spectra. The magnetic field increases from left to right.

the large 22.5-G coupling was assigned to two equivalent protons in the alcoholic methyl group; therefore, the quartet due to three equivalent protons likely arises from the acid methyl group. In order to verify these results, the deuterated analogue CH₃CO₂CD₃ was investigated. As expected, the spectrum for the $CH_3CO_2CD_3$ cation, shown in Figure 1B, shows the collapse of the large 22.5-G couplings due to two protons and the appearance of 3.5-G couplings due to two deuterons. The magnitude of the splittings is that expected from the ratio of the gyromagnetic moments of hydrogen and deuterium. A computer simulation of this spectrum (shown as the lower tracing of Figure 1B) assuming isotropic couplings of 3.5 G for two deuterons and 5.2 G for three protons results in a good fit to the experimental spectrum. An interesting feature of these results is that the coupling to three equivalent protons in the acid methyl group indicates this methyl group is undergoing free rotation whereas the coupling to only two of the

⁽¹³⁾ Wanatabe, K.; Nakatama, T.; Motti, J. J. Quant. Spectrosc. Radiat. Transfer 1962, 2, 369.

⁽¹⁴⁾ Meot-Ner (Mautner), M. J. Phys. Chem. 1980, 84, 2724.
(15) Clark, T. J. Comput. Chem., in press.



Figure 2. (A) First-derivative ESR spectrum of the deuterated ethyl formate π -cation at 128 K after γ -irradiation of 1% (mol/mol) solution in CFCl₃ at 77 K. (B) ESR spectrum of methyl-deuterated analogue under similar conditions, showing collapse of couplings in the π -cation due to deuteration. In both cases we are presenting the best-resolved spectrum of the stable π -cation, hence the different temperatures. See Figure 1 caption for explanation of hash marks.

three alcoholic methyl group protons indicates that this methyl group is not rotating on an ESR time scale. The ESR spectra do not indicate any rotation of this group even at 160 K, implying that there is an unusually large barrier to rotation (>8 kcal) for this group. The nature of the couplings in the methyl acetate cation indicates that it is a π -cation rather than a σ -cation.⁷ The equivalence of the two proton couplings in the frozen methyl group, as well as the large barrier to rotation of the methyl group, can be explained by an internal bonding between the methyl group and the carbonyl oxygen, which holds the cation in the ring structure shown in Figure 1A,B.

In our previous work with the methyl formate π -cation, we found evidence for a similar large barrier to rotation of the alcoholic methyl group.⁷ In addition, large barriers to rotation of terminal methyl groups are observed in cations of the ethyl esters described below.

The methyl acetate cation radical persists until the softening point of the matrix at which the ESR signal disappears. In more concentrated samples we found the deprotonated radical, $\cdot CH_2CO_2CD_3$, at these elevated temperatures (160 K).

Ethyl Formate. The ESR spectrum of the π -cation radical formed at 77 K from the γ -irradiation of samples containing 1% $DCO_2CH_2CH_3$ and annealed to 128 K is shown in Figure 2A. The spectrum of the methyl-deuterated analogue, DCO₂CH₂CD₃, at 148 K is shown in Figure 2B. The spectrum in Figure 2A arises from couplings of 22.3 G due to two protons and 9.8 G also due to two protons. As can be seen in Figure 2B, deuteration of the methyl protons causes a dramatic change in the ESR spectrum. The two 10-G hyperfine couplings disappear; these couplings are therefore unambiguously assigned to the γ -methyl protons. These couplings are unusually large for γ -protons and either indicate an efficient hyperconjugative mechanism or result as a direct effect of the intramolecular π^* -bonding. The second unusal feature of the γ -couplings is that only two of the three methyl group protons have observable coupling. This is strong evidence that the methyl group is not rotating and is "locked" (partially as it turns out from the discussion below) on a ESR time scale. Further, we note that the couplings found for both the β - and γ -protons are consistent with only a single relatively rigid and thermodynamically stable structure. In fact, the terminal methyl protons give no evidence



Figure 3. Change in the first-derivative ESR spectrum of deuterated ethyl formate π -cation with temperature, showing motional effects on the spectrum. This change is reversible.

of rotation even at 160 K, the matrix softening point. The structure shown in Figure 2 which suggests a bonding between the terminal methyl group and the carbonyl oxygen is, again, considered a reasonable possibility.

The ESR spectra of ethyl formate, $HCO_2CH_2CH_3$, radical cation are about the same as that of the acyl-deuterated analogue, $DCO_2CH_2CH_3$, except that additional line broadening was observed in the protonated compound. This broadening must arise from the acyl proton. An analysis of the spectra of these species suggests the acyl proton coupling is in the range of 3-4 G.

Although the terminal methyl group protons show no evidence for free rotation even at 160 K, they do give evidence for a reversible conformational interconversion at lower temperatures. In Figure 3A-D we show the spectra found on warming the ethyl formate (DCO₂CH₂CH₃) π -cation from 77 to 128 K. This change in spectra with temperature is found to be reversible. In contrast, however, the sample of the methyl-deuterated ethyl formate (DCO₂CH₂CD₃) cation did not show any change in the spectrum with temperature (once the sample had been annealed to 130 K). This argues quite convincingly that the change in spectra with temperature observed in Figure 3 results from a change in couplings from only the terminal methyl group. Analysis of the spectrum found at 77 K (Figure 3A) shows that it is consistent with two β -protons at 22.3 G and one γ -proton at 16 G. The intermediate temperature spectra (at 106 and 112 K) give evidence for a time-dependent averaging process, in which the 16-G proton averages with one of the other γ -protons with small coupling (ca. 3 G) to produce two equivalent γ -protons with ca. 10-G coupling.^{16,17} Computer simulations of the spectra taken at 77, 106, 112, and 128 K, employing modified Bloch equations for a twojump process, give a good fit to the experimental spectra found at these temperatures.¹⁶ These simulations are shown in Figure 4A-D. The splittings employed were 22.3 G (2 H), 16 G (1 H), and 3 G (1 H). The jump interconverted the 16- and 3-G splittings. The correlation time, τ , for the jump process is given in Figure 4 for each of the simulations and varies from 3×10^{-7} to 2×10^{-9} s. A straightforward Arrhenius analysis of ln $(1/\tau)$ vs. 1/T (K) results in a barrier to motion of 1.7 ± 0.5 kcal/mol. We envision that the actual process which occurs as a torsional oscillation of the methyl group rather than a free rotation. This barrier is considered further evidence for formation of a ring structure through some type of internal bonding.

Continued warming of the ethyl formate π -cation at 160 K resulted in a deprotonation reaction to produce the HCO₂CHCH₃ radical perhaps by an ion-molecule reaction.¹⁸ The reaction

⁽¹⁶⁾ Suryanarayana, D.; Sevilla, M. D. J. Chem. Phys. 1980, 72, 1325. Suryanarayana, D.; Sevilla, M. D. J. Phys. Chem. 1979, 83, 1323.

⁽¹⁷⁾ The third γ -proton coupling is presumed to be small (<4 G) and not involved in the averaging process.



Figure 4. Computer simulations of the first-derivative ESR spectra of deuterated ethyl formate π -cation, showing motional effects on the spectra (see Figure 3). The simulations employed the modified Bloch equations for a two-jump process; τ is the correlation time for the jump process. The residual peak to peak line width used was 4 MHz.

occurred somewhat more readily than that found for methyl acetate and is likely a result of the increased stability of the secondary radical produced from the ethyl formate π -cation over the primary radical produced by the deprotonation of the methyl acetate π -cation.

 π -Cation Radicals of Methyl Propionate, Ethyl Acetate, and Ethyl Propionate. We have also observed the ESR spectra of the methyl propionate, ethyl acetate, and ethyl propionate π -cation radicals. The splittings reported in Table I are given for the best spectra found after annealing to the various temperatures shown in the table. The results for these larger ester cations were complicated by their ready tendency to deprotonate bimolecularly by an ion parent molecule reaction; as a consequence low concentrations were employed to stabilize the cations.

The ESR spectrum for methyl propionate cation (0.5 mol %) at 77 K was a 25-G triplet. Warming to 125 K improved the resolution and produced a further coupling of ca. 7 G due to a single proton. Experiments with $CH_3CH_2CO_2CD_3$ gave only a unresolved singlet showing that the triplet in the protonated ester arises from the alcohol side methyl group. The 7-G doublet is therefore assigned to a single proton on the first methylene of the propionate group.

The results for ethyl propionate were similar to those found for ethyl formate. Again, a temperature dependence was found which resulted in similar high-temperature couplings (Table I); however, the low-temperature spectra suggested that both the β and γ -protons were involved in the averaging process. Results for CH₃CH₂CO₂CH₂CD₃ confirmed that the couplings observed in the cation of ethyl propionate arose from the alcoholic ethyl group.

Only the results for ethyl acetate can be considered somewhat unusual. In this case the 125 K spectrum showed evidence for four couplings each due to one proton (Table I). Further warming showed evidence for alteration in these couplings perhaps by an averaging process. Experiments with the deuterated compound $CD_3CO_2CH_2CH_3$ gave results identical with those of the protonated compound, indicating the acid-methyl coupling is quite small.

Deprotonation Reactions at 77 K. We have found that the ester cation radicals of propyl formate, propyl acetate, and propyl propionate as well as the butyl esters deprotonate from specific sites on the alcohol side alkyl group at 77 K. Concentration studies at low concentrations show that this is not due to an ion-parent molecule reaction¹⁸ and is a result of internal deprotonation to the ester functional group or deprotonation into the matrix.

Studies of the methyl, ethyl, and propyl butyrates show that the free radicals are produced only on the butyrate alkyl group at 77 K. We believe these results can be explained on the basis of the relative ionization energies of the ester functional group and the alkyl substituent. This work will be detailed in the future.

Discussion

Ester Cation π -Spin Density Distribution. The hyperfine couplings observed for methyl formate and methyl acetate cations allow for an estimate of the π -spin density distribution in the ester group. Previous work with oxygen-centered radicals suggests large couplings from β -protons.¹⁹ For example, in the well-known relation between dihedral angle (θ) and β -proton splitting (A_{β}), $A_{\beta} = B\rho^{\pi} \cos^2 \theta$, the value of the constant B is about 100 G for a number of radicals with spin density (ρ^{π}) on a single oxygen.¹⁹ Employing this value of B, $\theta = 30^{\circ}$, and $A_{\beta} = 23$ G for the methyl ester cations, we find a spin density of 0.31 on the ether oxygen. The 5.6-G coupling from the acyl hydrogen in methyl formate and the 5.2-G coupling from the rotating methyl group in methyl acetate suggest carbonyl carbon π -spin densities of (-)0.21 and (-)0.13, respectively.²⁰ The spin density is presumed to be negative due to the allylic nature of the ester cation. Since the remaining spin density must lie principally on the carbonyl oxygen in these radicals, this approach suggests about 0.8 of an unpaired spin at this site.

INDO calculations of the spin density distribution give a somewhat different picture of the π -spin density distribution.⁷ For methyl formate the calculation predicts π -spin densities of 0.78 at the ether oxygen, -0.42 at the carbonyl carbon, and 0.57 at the carbonyl oxygen. The fact that the calculation correctly predicts the magnitude of the β -proton couplings lends some weight to the predicted spin densities, although the negative spin density is likely too large. The value of the constant *B* suggested from the INDO spin density of 0.78 is considerably smaller (40 G) than found for radicals with spin density on a single oxygen (ca. 100 G).

Only oxygen-17-labeling studies will settle this point of disagreement. However, it is clear from both predictions that substantial spin density resides on both ester oxygens. Thus, the ester cations can be viewed as a hybrid of the valence structures, I and II, shown below. This hybrid is best represented by structure III.



It is interesting to note that radicals with spin density localized on a single oxygen such as alkoxy radicals (RO·) have a large gvalue anisotropy while those with delocalized π -systems such as the three-centered π -system (-OCH₂O-) found in acetal radical cations show more isotropic g values.² The isotropic g value (2.0025) found for the ester cations in this work is considered further evidence for the delocalized spin density shown in structure III.

Barriers to Methyl Group Rotation—Intramolecular π^* -Bonding. The high barriers to rotation of the methyl groups in the ester π -cations is an intriguing problem. Methyl group barriers to rotation in free radicals are usually in the range 1–5 kcal/mol; $^{16,21-23}$ however, the alcohol side methyl groups in the π -cations of methyl formate, methyl acetate, and methyl propionate as well as the terminal methyl groups in the π -cations of ethyl formate and ethyl propionate give evidence for substantially greater barriers. A logical explanation for the high barriers to rotation

- (20) This calculation assumes the following values for the constant Q in the McConnell relation $A = Q\rho$: $Q(CH_3) = 40$ G and Q(H) = -27 G. (21) Suryanarayana, D.; Sevilla, M. D. J. Phys. Chem. **1980**, 84, 3045.
- (21) Fassenden, R. W.; Schuler, R. H. J. Chem. Phys. 1963, 39, 2147.
 (23) Chen, K. S.; Krusic, P. J.; Meaken, P.; Kochi, J. K. J. Phys. Chem.
- 1974, 78, 2014 and references therein.

⁽¹⁸⁾ Shiotani, M.; Nagata, Y.; Tasaki, M.; Sohma, J.; Shida, T. J. Phys. Chem. 1983, 87, 1170 and references therein.

⁽¹⁹⁾ Bernhard, W. A.; Close, D. M.; Hüttermann, J.; Zehner, J. J. Chem. Phys. 1977, 67, 1211.

is that there is internal bonding between the alkyl group and the ester functional group. The fact that in methyl acetate one methyl group was found to rotate while the other was not shows that the barrier is specific and likely a result of weak bonding to the carbonyl portion of the ester functional group. For the methyl esters, two possible bonding structures which result in ring formation are shown below, where R = H, CH_3 , or CH_2CH_3 .



In the discussion which follows, we present the factors which lead to the acceptance of structure V as the most reasonable structure for the methyl ester cations.

Structure IV may result from two rather different bonding situations. In the first case, the dotted line represents an electron-deficient σ^* -bond in which stabilization of the bond occurs due to removal of an electron from an antibonding σ^* -MO. However, this bond would place a large amount of unpaired spin density on the bonded hydrogen and little or no spin density on the other two hydrogens which are π in nature. This is inconsistent with our experimental results which show two large equivalent hyperfine couplings to two protons on the methyl group and only small coupling to the third. Thus, the σ^* -bond concept is rejected.

The other possibility for structure IV is one in which a bond analogous to a standard hydrogen bond is formed by electrostatic interactions. It must be remembered, however, that in ester cations the carbonyl oxygen has a reduced electron density due to the electron removal.⁷ Thus, structure IV does not appear to be a reasonable representation of the methyl ester cation radicals.

In structure V, we suggest that in the cation an electron-deficient intramolecular π^* -bond forms in which stabilization occurs to removal of an electron from an antibonding π^* -MO. This stabilization occurs for the cation only and not for the parent ester, so both the bonding and antibonding π -MOs involved in the new bond form only as the cation is produced. The conformation in structure V is that of the parent ester,²⁴ which permits the cation to form at 77 K without any molecular reorientation. As described in the discussion on bonding (below), the π -nature of the cation also places unpaired spin density on the two out-of-plane methyl hydrogens and not on the third in-plane methyl hydrogen, in agreement with our observed pattern of proton hyperfine couplings.

The nature of the bonding in structure V can be described in a straightforward manner by the group orbital method of Jorgensen and Salem.¹² This method, which is based on rigorous applications of symmetry and quantum mechanics, describes seven localized CH₃ group orbitals which are formed from the four highest carbon atomic orbitals and three hydrogen 1s orbitals. These seven group orbitals are then used to construct molecular orbitals for molecules in which the methyl group is present. One of the group MOs is used to bond the carbon of the methyl group to another carbon and does not concern us. The other six are involved in C-H bonding and are directly related to the internal bonding we postulate. These six orbitals can be divided into three sets, one set of σ -symmetry, one set of π -symmetry, and one set of pseudo π -symmetry.

Internal π^* -bonding occurs through interaction of the ester π -system and the occupied methyl group orbital of rigorous π -symmetry as pictured in Figure 5. The methyl group orbital involved is spatially appropriate for this interaction, both with regard to its symmetry and location in space. The methyl group π -orbital centered on two hydrogens is approximately 1.8 Å away from the carbonyl π -electrons, providing a reasonable opportunity for orbital overlap; a distortion of the molecular structure may also occur to allow for stronger bonding.^{25,26}



Figure 5. This figure qualitatively depicts the formation of a π^* -bond from the mixing of the methyl group orbital of rigorous π -symmetry with the π -HOMO of the ester functional group. See text for a complete discussion.

The interaction described above is energetically stabilized due to the electron-deficient nature of the system. In the parent molecule, both the new bonding MOs and antibonding MOs formed would be fully occupied and no net stabilization would occur. In the radical cation, there is, essentially, loss of an electron from the antibonding MO; hence stabilization occurs.

For the ethyl esters, structures VI and VII, which are analogous



to IV and V, are the two most likely bonding structures, where R = H, CH_3 , or CH_2CH_3 . For the reasons stated above for the methyl esters, structure VI is ruled out as a reasonable representation of the ethyl ester cations. Using arguments identical with those put forth for the methyl esters, we suggest that an electron-deficient intramolecular π^* -bond forms, resulting in the ring structure VII. In this case, however, it is likely molecular conformational change occurs when the π^* -bond is formed.

The bonding of the two methyl protons to the carbonyl oxygen provides an explanation of the large γ -proton splittings found for the ethyl esters as well as the high barriers to rotation. The temperature dependence in these γ -splittings is clearly a result of a torsional motion of the terminal methyl group. The 1.7-kcal barrier found for this motion points to ring formation and, interestingly, compares favorably with ring inversion barriers in tetrahydrofuran radical cation (1.65 kcal)⁵ and cyclopentane carboxylic acid neutral radical (1.4 kcal).¹⁶

The internal bonding in these electron-deficient structures is a reasonable and expected result of the reorganization of the molecule after electron loss.²⁷ In other structures such as alkane cations the terminal methyl groups also show unusual barriers to rotation.^{1,6,9,10} Iwasaki has explained the barrier for ethane cation as resulting from the formation of a diborane-like structure.¹⁰ This form of electron-deficient internal bonding might contribute to the barrier in the ethyl ester cations. Thus, internal bonding within the alkyl group could then explain the large barrier to rotation of the terminal methyl group in ethyl ester cations and could argue for another structure with the methyl group away from the carbonyl group. However, since the ethane cation shows internal rotation at 77 K, the barrier for this radical is apparently far less than that in ethyl formate cation which shows no terminal methyl rotation even at 160 K. This and the fact we observe a torsional barrier lead us to conclude that only electron-deficient bonding to the carbonyl oxygen provides a reasonable explanation for the phenomenon observed.

⁽²⁴⁾ Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A.
"Conformational Analysis"; Interscience: New York, 1965.
(25) Davidson, R. B.; Miyagawa, I. J. Chem. Phys. 1970, 52, 1727.

⁽²⁶⁾ Becker, D. Ph.D. Thesis, University of Washington, Seattle, WA, 1976.

⁽²⁷⁾ We note that many INDO-MO calculations were performed for structures IV-VII. For methyl formate complete energy minimization calculations predicted strong intramolecular bonding. In the case of ethyl formate calculations also gave evidence for intramolecular bonding. However, for both esters the calculations predicted σ^* -bonding not π^* -bonding indicated by the experimental splittings. Clearly, more sophisticated calculations are needed to elucidate the internal bonding and electronic structure of the ester cations.

Acknowledgment. We thank R. L. Stern, J. Gendell, and M. C. R. Symons for a number of helpful suggestions. In addition, we thank the Office of Health and Environmental Research of the U.S. Department of Energy (Contract No. 76-EVO-2364) and the U.S. Department of Agriculture (Contract No. 53-32u4-1-224) for support of this research.

Registry No. Methyl formate cation radical, 82188-89-4; methyl

acetate cation radical, 76023-58-0; methyl propanoate cation radical, 73834-00-1; ethyl formate cation radical, 76402-44-3; ethyl acetate cation radical, 73889-89-1; ethyl propanoate cation radical, 89144-64-9; methyl deuterioformate cation radical, 89144-65-0; methyl- d_3 acetate cation radical, 89144-66-1; methyl- d_3 propanoate cation radical, 89144-67-2; ethyl deuterioformate cation radical, 89144-68-3; ethyl- $2,2,2-d_3$ deuterioformate cation radical, 89144-69-4; ethyl acetate- d_3 cation radical, 89144-70-7.

Resonance Raman Studies of Pulse Radiolytically Produced *p***-Aminophenoxyl Radical**¹

G. N. R. Tripathi^{*} and Robert H. Schuler^{*}

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (Received: August 15, 1983)

The p-aminophenoxyl radical produced in the pulse radiolytic oxidation of p-aminophenol in aqueous solution has been examined by time-resolved resonance Raman methods. Eight Raman bands of fundamental vibrations were observed at microsecond times and at radical concentrations of $\sim 10^{-5}$ M by excitation in the moderately strong absorption band of this radical at 444 nm ($E = 6800 \text{ M}^{-1} \text{ cm}^{-1}$). This radical decays rapidly by second-order processes ($2k = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) so that at times longer than milliseconds the residual signals are very weak. The most intense Raman band of this radical, observed at 1636 cm⁻¹, is ascribed to the Wilson 8a ring stretching mode and is similar in frequency to this mode in p-benzosemiquinone radical anion (1620 cm⁻¹). The mixed CO/CN stretching frequency (1434 cm⁻¹) is also very similar to that of the analogous mode in p-benzosemiquinone. This radical exhibits no strong Raman bands in the region of 1510–1520 cm⁻¹ as do most other substituted phenoxyl radicals. Deuterium substitution of the NH₂ group shows that a band at 1673 cm⁻¹ in the protonated radical is due to the symmetrical NH₂ bending vibration. Interestingly, this deuterium substitution results in small increases in the frequencies of the CO/CN and ring stretching vibrations. The Raman data show very clearly, in agreement with conclusions from ESR data, that the structure of p-aminophenoxyl radical is more similar to that of a semiquinone than it is to that of a phenoxyl radical. The high second-order rate constant observed for decay, however, indicates that the NH₂ group contributes significantly to modifying the redox properties of this radical.

We have previously reported² preliminary observations on the microsecond time scale of Raman signals from *p*-aminophenoxyl radical produced in the pulse radiolytic oxidation of *p*-aminophenol in basic solution. We present here a more complete study of the Raman spectrum of this radical obtained in time-resolved experiments which shows very clearly, in accord with our previous comments and the conclusions from ESR data, that the electronic structure of this radical is more similar to that of *p*-benzosemi-quinone radical anion than it is to that of a substituted phenoxyl radical. This similarity, together with appropriate symmetry considerations, forms the basis for interpreting the resonance Raman spectrum of *p*-aminophenoxyl radical in this paper.

Experimental Section

Various experimental aspects of our time-resolved resonance Raman studies on intermediates present in pulse radiolysis experiments have been described in previous publications.²⁻⁶ Currently, the configuration being used consists of a pulsed 2-MeV electron Van de Graaff as the radiation source, a Lambda-Physik 2001 dye laser pumped at 308 nm with a Lambda-Physik 102 eximer laser as the Raman excitation source, a Spex 0.85-m spectrograph as the dispersive element, and a Princeton Applied Research 1215 OMA II optical multichannel analyzer system using a gated intensified photodiode array as the detector. Time resolution is obtained by delay of the laser pulse with respect to the electron pulse. With this configuration we have been able to obtain almost 2 orders of magnitude improvement in signal-

(2) Tripathi, G. N. R.; Schuler, R. H. J. Chem. Phys. 1982, 76, 4289.
 (3) Tripathi, G. N. R.; Schuler, R. H. J. Chem. Phys. 1982, 76, 2139.

(4) Tripathi, G. N. R.; Schuler, R. H. J. Phys. Chem. 1983, 87, 3101.
 (5) Schuler, R. H.; Tripathi, G. N. R.; Prebenda, M.; Chipman, D. M. J.

Phys. Chem. 1983, 87, 5357.

to-noise ratio over our initial studies, as was previously estimated² to be available in this type of experiment. Signals of the more intense lines of *p*-aminophenoxyl radicals can now be observed at concentrations of $\sim 10^{-6}$ M even though the extinction coefficient is only 7000 M⁻¹ cm⁻¹. These improvements make it possible to carry out experiments at times down to ~ 10 ns and under pulse radiolysis conditions similar to those used in optical absorption studies.

An irradiation pulse of 0.5 A at 2 MeV for a period of 10 ns or longer was used with the electron beam tightly focused (1 mm^2) on the center of the Raman cell. In most cases doses were limited to the order of 2000–10000 rds/pulse (initial radical concentration $(1-5) \times 10^{-5} \text{ M}$) to minimize absorption of the exciting light within the Raman cell. Experiments were carried out at a repetition frequency of 7.5 s⁻¹.

The Raman cell was 5 mm long and had a 3-mm i.d. (~ 0.05 cm³). In most cases flow rates of the order of 2 cm³/s were used so that the solution was replenished between pulses. The exciting light and Raman emission passed through only ~ 2 mm of solution so that at radical concentrations of $\sim 10^{-5}$ M the former was attenuated by only a few percent and the latter by even less. At higher radical concentrations absorption of the exciting light within the Raman cell can become important and significant corrections must be applied when concentration estimates are desired as in, for example, kinetic experiments.

Most of the present studies were carried out using Coumarin-120 in the dye laser which produced at 444 nm a pulse 8 ns wide with an energy of ~ 5 mJ. The intensity is an order of magnitude greater than that available from the N₂-pumped dye laser used in our preliminary study and to a large extent accounts for the noted increase in sensitivity.²

The Raman emission was collected 90° to the laser beam with an 8-cm diameter f/1.6 lens and focused on the entrance slit of the Spex 1402 spectrograph. The spectrograph has an aperture of f/7.5 and a 1800 grove/mm halographically ruled grating used in first order. At 444 nm the dispersion of the spectrograph in

⁽¹⁾ The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2505 from the Notre Dame Radiation Laboratory.

⁽⁶⁾ Tripathi, G. N. R.; Schuler, R. H. Chem. Phys. Lett. 1983, 98, 594.