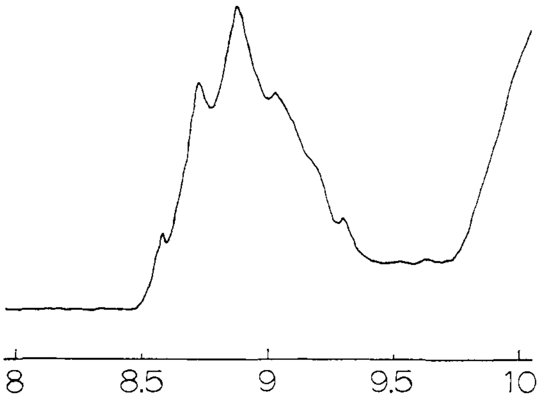

Figure 5. The 8–10-eV region of the photoelectron spectrum of adamantanone.

molecular skeleton increased; the values for cyclooctanone were 9.09 and 10.3 eV, respectively. Vibrational structure was observed in the first band also, and frequencies of 740 and 1267 cm^{-1} were reported.[25] The photoelectron spectrum of adamantanone in the current work exhibited vibrational structure in the first band (see Figure 5) with $\nu = 1210\ cm^{-1}$, which can be assigned to the C=O stretch for the ion. The vertical I_1 adamantanone is 8.88 eV which is lower than that[25] for cyclooctanone, as would be expected for the larger ring system. Furthermore, MINDO/1 predicts that the highest occupied MO for adamantanone is located predominantly on the carbonyl oxygen, although there is predicted substantial delocalization of this MO throughout the molecule. Thus it is quite certain that I_1 for adamantanone corresponds to an oxygen "lone-pair" electron. The I_2 for adamantanone (9.74 eV) must then refer to the inductively destabilized "σ onset." It should be emphasized, however, that the "lone-pair" MO corresponding to I_1 is substantially delocalized for this ketone, as can be inferred from the rather extensive vibrational structure and the low value of ν for the ionic state. The first band in the spectrum of 2,6-adamantanedione also exhibits vibrational structure with $\nu = 1210\ cm^{-1}$ (and also 550 cm^{-1}). The adiabatic and vertical first ionization potentials of this diketone are several tenths of an electron volt higher than those for adamantanone but lower than the values for adamantane. This ionization process can be assigned once again to the nonbonding MO confined mainly on oxygen. However, the rather large shift to higher ionization energy shows that this "nonbonding" MO is quite delocalized, and the ionic state is destabilized inductively by the presence of a second carbonyl group.

Acknowledgments. The authors are grateful for partial financial support from the National Science Foundation and the Cleveland Foundation. They also thank Mr. Paul Bright for his assistance in maintaining the photoelectron spectrometer. Helpful discussions with Professor M. J. S. Dewar and W. Goodman of the University of Texas and Professor Kerro Knox of Cleveland State University are also gratefully acknowledged.

Photochemistry of Propionaldehyde in Solution Studied by Electron Spin Resonance and CIDNP

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Abstract: The photolysis of propionaldehyde in solution has been studied by means of electron spin resonance and proton nuclear magnetic resonance spectroscopy. The nmr spectrum obtained during irradiation indicates that a number of compounds are formed with their protons spin polarized. Using a radical pair model to account for the nuclear spin polarization, it is possible to suggest photochemical reaction steps to account for the observed nmr spectrum. By means of radical trapping experiments using carbon tetrachloride, it is possible to decide which components are formed by primary photochemical steps and which are derived by subsequent steps. Quenching by nitric oxide supports the proposal that the primary steps occur *via* the excited triplet electronic state. Among these steps are α cleavage and bimolecular hydrogen abstraction.

Recently the photochemistry of acetaldehyde[1] and pivalaldehyde[2] in solution was studied by means of chemically induced dynamic nuclear spin polarization (CIDNP). For acetaldehyde, the observed spin polarization was explained by a bimolecular primary step in which an acetaldehyde molecule in an excited triplet state removes the carbonyl hydrogen from a ground state acetaldehyde molecule. In contrast, the CIDNP results for pivalaldehyde were explained by a unimolecular primary step which involved α cleavage *via* a triplet excited state to give the *tert*-butyl and formyl radicals.[3] Furthermore, variation of the solvent seems to have no effect on the outcome for either of these compounds.

For these reasons we have undertaken a study of the photochemistry of propionaldehyde to ascertain if

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[1] B. Blank and H. Fischer, *Helv. Chim. Acta*, **56**, 506 (1973).

[2] H. Chen, A. Groen, and M. Cocivera, *Can. J. Chem.*, **51**, 3032 (1973).

[3] A similar step has been proposed for α-aryl aldehydes, see K. Schaffner, H. Wolf, S. Rosenfeld, R. Lawler, and H. Ward, *J. Amer. Chem. Soc.*, **94**, 6553 (1972).

both primary steps can be detected for this compound. This study involved the use of CIDNP and electron spin resonance (esr) spectroscopy. Our results provide evidence for the occurrence of both primary steps for propionaldehyde. In addition, studies using propionaldehyde-*2,2-d_2* help to clarify the nature of the polarization step for the carbonyl proton. The esr results provide support for the bimolecular hydrogen abstraction step since the $CH_3CH_2\dot{C}OH$ radical in addition to the $CH_3CH_2\cdot$ radical is detected during irradiation.

Experimental Section

Chemicals. Perfluoromethylcyclohexane (Pierce Chemical), 3-pentanol (Aldrich Chemical Co.), 1-propanol (Baker Chemical Co.), 3-pentanone (Aldrich Chemical Co.), acetoin (Baker Chemical Co.), nitric oxide (Matheson Gas Co.), and carbon tetrachloride were used without purification. Propionaldehyde (Baker Chemical Co.) and propionaldehyde-*2,2-d_2* (Merck Sharp and Dohme) were distilled once at atmospheric pressure, bp 49°.

Nmr. The proton nmr spectra at 100 MHz were obtained at 15° using a Varian HA-100-15 spectrometer which we have modified to operate on a time-sharing mode. In this mode, we are able to use a quartz probe which allowed direct irradiation of the sample while the nmr spectrum was obtained. This probe was built in our laboratory and the details are given elsewhere.[4] The nmr spectra were obtained before, during, and after irradiation. The radiation source was a 1000-W Hanovia mercury-xenon lamp. For some of the experiments, a filter was employed to allow transmission of radiation having wavelengths greater than 310 nm. The detailed structure of the spectrum was the same with and without the filter. However, larger intensities were obtained without the filter.

Esr. The electron spin resonance spectra were obtained at 9.6 GHz (X band) using a Bruker BE-414 spectrometer. These spectra were obtained during irradiation with the full spectrum of a 1000-W mercury-xenon lamp at ambient temperature. The spectra were observed for flowing solutions but not for static solutions. These solutions were flowed at about 1 ml/sec using a peristaltic pump.

Results and Discussion

Esr. In Figure 1 is illustrated the esr spectra obtained during irradiation of 9% propionaldehyde in benzene. This spectrum was obtained at ambient temperature while flowing the solutions through the cavity at a rate of 1 ml/sec. In this spectrum the strong lines are due to two radicals. For one radical, the *g* factor is 2.0032, and the hyperfine splittings are due to three protons in equivalent sets, 2:1, with coupling constants being 21.4 and 15.1 G, respectively. We assign this spectrum to the radical $CH_3CH_2\dot{C}HOH$, a, since these parameters are identical with those measured for this radical previously.[5] The hyperfine coupling constant for CH_3 hydrogens of this radical was found to be 0.46 G at −40° whereas the value for the OH hydrogen appears to be 0.[5] For the other radical, the *g* factor is 2.0026, and the hyperfine splittings are due to five protons in equivalent sets, 3:2, with the coupling constants being 26.9 and 22.4 G, respectively. These parameters are identical with those for the ethyl radical, b.[6] As can be seen in Figure 1, the spectrum of a is weaker than the one for b. However, when *tert*-butyl alcohol is the solvent, the reverse is true. This solvent effect could reflect the relative stabilities of these radicals, in each solvent, or it could indicate a solvent dependence for the relative rates of formation of these radicals.

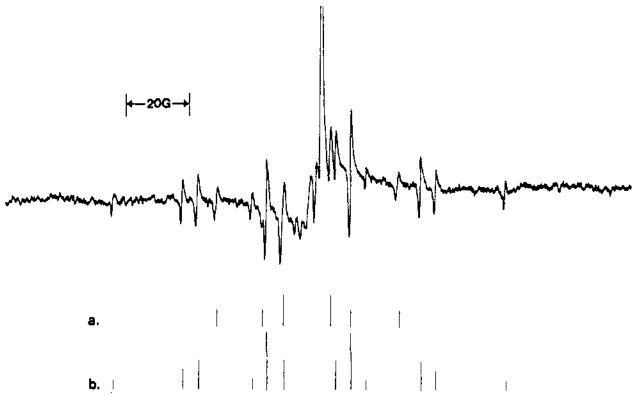

Figure 1. Esr spectrum of 9% propionaldehyde in benzene at room temperature obtained during irradiation with the full spectrum of a mercury-xenon lamp. The spectrum is analyzed as a superposition of the spectrum (stick figure a) of $CH_3CH_2\dot{C}HOH$ and the spectrum (stick figure b) of $CH_3CH_2\cdot$. The large line in the center is a cell signal.

The formation of radical $CH_3CH_2\dot{C}HOH$ can be explained by the following mechanism (eq 1) where R

$$\mathrm{RCOH} \xrightarrow{h\nu} \mathrm{RCOH}^* \qquad (1)$$

$$\mathrm{RCOH}^* + \mathrm{RCOH} \longrightarrow \mathrm{R\dot{C}HOH} + \mathrm{RCO}\cdot$$

signifies the ethyl group. According to this mechanism a propionaldehyde molecule in an excited electronic state removes a hydrogen atom from a propionaldehyde molecule in the ground state. This mechanism is similar to the one proposed for acetaldehyde.[1] The spin multiplicity of the excited state involved in this reaction is left unspecified, since the esr results provide no information concerning this aspect. However, as discussed below the nmr results indicate that the triplet excited state is involved.

The formation of the ethyl radical may occur *via* decarbonylation of $RCO\cdot$ formed according to eq 1 or by another mechanism involving homolytic α-bond cleavage *via* an excited state of propionaldehyde to give $CH_3CH_2\cdot$ and $\cdot COH$. While the esr results cannot be used to distinguish between these mechanisms, the nmr results can.

As is evident in Figure 1, we could not detect any esr signals which might be due to the propionyl radical. Since our CIDNP results presented below indicate that this radical takes part in reactions with the radicals observed by esr, the signal for this radical may be hidden by the cell signal, and/or the lifetime for this radical is too short for the esr time scale but not too short to prevent reaction with other radicals.

Nmr. During the irradiation of propionaldehyde under various conditions, transient nmr spectra were obtained. These spectra consist of both emission and enhanced absorption lines. Many of these lines either disappear or are reduced in intensity when irradiation is stopped. The interpretation of this phenomenon is based on a model in which non-Boltzmann nuclear spin polarization occurs as a result of reaction *via* a radical pair.[7]

Details of the theory used to calculate the nuclear spin polarization based on this model have been given

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(4) M. Cocivera, M. Tomkiewicz, and A. Groen, *J. Amer. Chem. Soc.*, **94**, 6598 (1972).

(5) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966).

(6) R. Fessenden and R. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(7) For a brief review, see R. Lawler, *Accounts Chem. Res.*, **5**, 25 (1972).

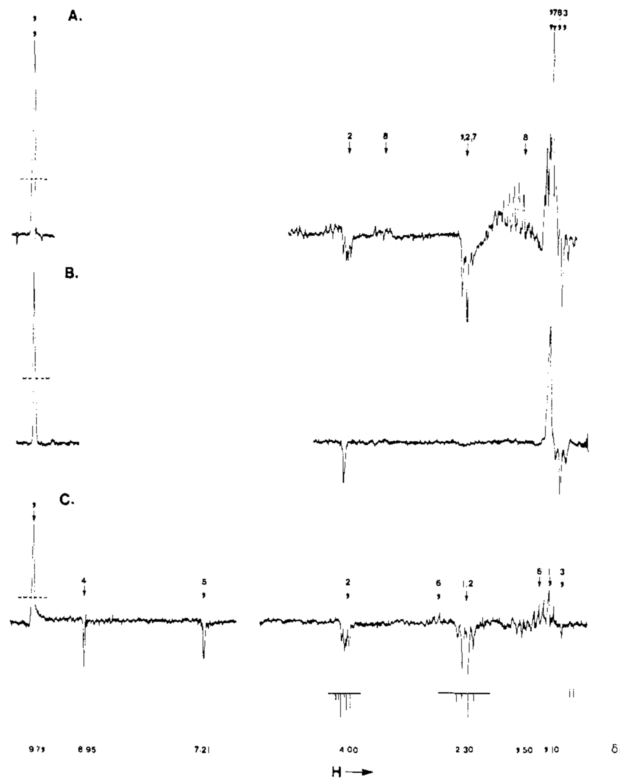

Figure 2. Nmr spectra obtained at 15° during irradiation of: (A) 0.2 M propionaldehyde in perfluoromethylcyclohexane; (B) 0.2 M propionaldehyde-*2,2-d*$_2$ in the same solvent; (C) 0.2 M propionaldehyde plus 0.1 M carbon tetrachloride in the same solvent. The sweepwidth is 1000 Hz. Part of the calculated spectrum for 4-hydroxy-3-hexanone, assuming formation *via* ii, is given at the bottom.

previously,[8] and only the final equations are given here. The nuclear spin polarization in a diamagnetic product is proportional to ($\rho_{SS}{}^{m} - \rho_{SS}{}^{j}$), where m and j indicate nuclear spin states, and ρ_{SS}, which is the diagonal density matrix element for the singlet spin state of the radical pair, is given by the expression

$$\rho_{SS}{}^{j} = \frac{(\alpha_{SS} + \mu_j(2 + \gamma)\alpha_{TT})/k_{-2}}{1 + \gamma + \mu_j(2 + \gamma)} \qquad (2)$$

In this equation, α_{SS} and α_{TT} depend on the nature of precursor for the radical pair: for singlet precursor $\alpha_{SS} = r$ and $\alpha_{TT} = 0$; for triplet precursor $\alpha_{TT} = r'/3$ and $\alpha_{SS} = 0$; and if two separate free radicals combine to form the radical pair, $\alpha_{TT} = \alpha_{SS} = r''/4$ where r, r', and r'' are the rates for formation of the radical pair. In addition, in eq 2 $\gamma = k_1/k_{-2}$, where k_1 is the rate constant for product formation from the radical pair and k_{-2} is the rate constant for dissociation of the radical pair; and μ_j is given by the expression

$$\mu_j = \frac{\mathbf{H}_{ST}{}^2/k_{-2}{}^2}{(1 + \gamma/2)^2 + 4J^2/k_{-2}{}^2 + (2 + \gamma)\mathbf{H}_{ST}{}^2/k_{-2}{}^2} \qquad (3)$$

In eq 3, J is the electron exchange integral, and $\mathbf{H}_{ST}$ is the off-diagonal matrix element of the spin Hamiltonian which mixes the singlet with the $M = 0$ state of the triplet manifold and is obtained from the expression

$$\mathbf{H}_{ST} = {}^1/_2\beta H_0(g_1 - g_2) + {}^1/_2\sum_l(A_1{}^l - A_2{}^l)\langle M_I|I_z{}^l|M_I\rangle \qquad (4)$$

In this expression β is the electron Bohr Magneton, H_0 is the strength of the external magnetic field, g is the isotropic electronic g factor, A is the electron nuclear coupling constant, M_I is the nuclear spin state, I_z is the z component of the nuclear spin operator, and the subscript and superscript label the electron and nucleus, respectively.

For the calculations, the g and A values for each radical are taken from esr data. The values used for J, k_{-2}, and γ are 10^8 Hz, 10^9 sec^{-1}, and 0.2, respectively, and although they are reasonable,[8] they are somewhat arbitrary. Consequently, absolute values for nuclear spin polarization could not be calculated. However, since the esr data are known, the calculated relative values are meaningful and very useful in understanding the photochemical reaction of propionaldehyde.

The nmr spectrum obtained during irradiation of 0.2 M propionaldehyde (**1**) in perfluoromethylcyclohexane[9] is given in Figure 2A. This spectrum was obtained using the full spectrum of the mercury–xenon lamp. Filtering the radiation to remove light of wavelength shorter than 310 nm reduces the intensity of the spectrum but does not change its details. The temperature in the nmr probe was maintained at 15°.

As is evident in this spectrum, a number of compounds have been formed during irradiation. With the exception of the CH_3–hydrogen resonance of **1** at 1.10 ppm (all chemical shifts are relative to TMS), all of the lines exhibit either enhanced absorption or emission, indicating non-Boltzmann nuclear spin polarization. Before discussing this spectrum in detail, it is convenient to consider the other spectra in Figure 2. Figure 2B illustrates the spectrum obtained for propionaldehyde-*2,2-d*$_2$ under the same conditions as used for Figure 2A. Note that all the lines observed around 1.55 ppm in Figure 2A are not observed in Figure 2B. The disappearance of these lines upon deuteration of the methylene group indicates that the hydrogens giving rise to these lines were originally methylene hydrogens in propionaldehyde. We will return to this spectrum below. In Figure 2C is illustrated the spectrum obtained under the same conditions as Figure 2A except that 0.1 M CCl_4 is present in the solution. Note that many of the lines in Figure 2A do not appear in Figure 2C. Since CCl_4 acts as a radical scavenger, this result indicates that the products responsible for these lines are not obtained from the radical pair(s) formed initially from the excited state of propionaldehyde. Thus, we have used Figure 2C to determine which products are formed with nuclear spin polarization *via* the initial radical pair.

On comparison of Figure 2A with Figure 2C, one can see that the lines labeled 1, 2, and 3 are common to both. We have assigned these spectra to propionaldehyde (**1**), 4-hydroxy-3-hexanone (**2**), and ethane (**3**). The chemical shifts and multiplicities of the resonances are given in Table I. The assignment of **1** is based on its nmr spectrum prior to irradiation. The assignment of **2** is based on the multiplicity of the resonances and the fact that the chemical shifts are comparable with those measured for acetoin, *i.e.*, methine hydrogen at 4.15 ppm, carbonyl methyl at 2.12 ppm, and carbinol

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[8] M. Tomkiewicz, A. Groen, and M. Cocivera, *J. Chem. Phys.*, **56**, 5850 (1972).

[9] As indicated above, the esr spectrum was obtained using benzene as the solvent. The fluorocarbon was not used because the aldehyde was not sufficiently soluble to provide a spectrum for publication. However, the results are similar for both solvents.

Table I. Assignment of Nmr Lines Observed during Irradiation of Propionaldehyde in Perfluoromethylcyclohexane

Resonance	Position[a]	Compd
1	9.71 s 2.30 q 1.10 t	Propionaldehyde
2	4.00[b] 2.30 q 1.77[c]	4-Hydroxy-3-hexanone
3	0.90 s	Ethane
4	8.95 s	Trichloroacetaldehyde[d]
5	7.21 s	Chloroform[d]
6	2.83 q 1.21 t	Propionyl chloride[d]
7	2.29 q 1.07 t	3-Pentanone
8	3.55[c] 1.42[e] 0.97 t	3-Pentanol

[a] Chemical shifts relative to TMS in ppm; singlet (s), triplet (t), and quartet (q). [b] Methine hydrogen, apparently a quartet. [c] Multiplet not sufficiently resolved. [d] Observed when CCl_4 present. [e] Quintet.

methyl at 1.38 ppm. Enhanced resonances for the methyl groups of **2** are not observed and the explanation will be discussed below. The carbinol methylene group of **2** should be observed around 1.4 ppm. We suggest that this resonance is hidden by other lines which are superimposed. The following mechanism is consistent with the polarization observed for **2** and with the observation of the $CH_3CH_2\dot{C}HOH$ radical by esr.

$$CH_3CH_2COH \xrightarrow{h\nu} CH_3CH_2COH^S$$

$$CH_3CH_2COH^S \longrightarrow CH_3CH_2COH^T$$

$$CH_3CH_2COH^T + CH_3CH_2COH \longrightarrow \underset{\text{ii}}{[CH_3CH_2CHOH\cdot \quad \cdot OCCH_2CH_3]^T} \qquad (5)$$

$$\text{ii} \longrightarrow \left[\begin{array}{l} \longrightarrow CH_3CH_2CHOH\cdot + CH_3CH_2CO\cdot \\ \longrightarrow \underset{\mathbf{2}}{CH_3CH_2CHOHCOCH_2CH_3} \\ \longrightarrow \underset{\mathbf{1}}{2CH_3CH_2COH} \end{array} \right.$$

According to eq 5, **2** is formed *via* radical pair ii, which has an excited triplet electronic state precursor. For the calculation of the spin polarization due to ii, we have used values of 2.0032 and 2.0005[10] for g factors of the radicals CH_3CH_2CHOH and CH_3CH_2CO, respectively. For CH_3CH_2CHOH, values of -15.1 and $+21.4$ G were used for A_α and A_β, respectively, and a value of 5.1 G was used for A_β for CH_3CH_2CO.[10] The signs for the A's are based on the signs used for very similar radicals obtained during the irradiation of acetaldehyde.[1] For both radicals, the value for A_γ is neglected since it is very small compared with the values of the other hyperfine coupling constants. Because A_γ is so small, no measurable polarization is expected for the methyl hydrogens of **2**, and none is found. The polarizations calculated for the 2-methylene hydrogens and the methine hydrogen of **2** are illustrated as stick figures below Figure 2C. Positive values are used for the indirect nuclear spin–spin coupling constants since vicinal couplings are involved. This applies to all compounds discussed in this paper. The polarization for the 5-methylene hydrogens has not been illustrated since sharp resonance lines have not been observed for them, presumably because of overlap with other resonance lines. The spectrum obtained during the irradiation of propionaldehyde-*2,2-d_2* also supports the conclusion that **2** is formed *via* ii since the methine hydrogen resonance appears as a single emission line under these conditions, as would be expected. The observation of the radical $CH_3CH_2\dot{C}HOH$ by esr during the irradiation of propionaldehyde provides additional support for the formation of ii *via* eq 5. Finally, the ratio of methylene to methine resonance intensity is smaller in the calculated spectrum than in the observed spectrum. This difference is consistent with the disproportionation path suggested in eq 5 (and also a step analogous to eq 6, below) to give **1**, since the methylene hydrogen resonance of **1** also occurs near 2.30 ppm, and emission is calculated for this resonance.

The enhanced absorption observed for the carbonyl hydrogen of **1** cannot be explained by eq 5 because the calculation predicts emission rather than absorption for this hydrogen. Blank and Fischer[1] have observed this conflict for the photolysis of acetaldehyde, also. For that system, these workers observed resonance lines which they assigned to the enol of acetaldehyde and consequently explained the enhanced absorption by the following step. The superscript F signifies a radical

$$[CH_3CHOH\cdot\ \cdot COCH_3]^{T,F} \longrightarrow CH_2CHOH + CH_3CHO \qquad (6)$$

pair formed from free radicals, *i.e.*, no appreciable interaction between the unpaired electrons before the radical pair is formed. While we observe resonance lines which may be attributed to the enol $CH_3CHCHOH$ (see Figure 2A around 4.2 ppm), we feel eq 6 cannot account totally for the polarization observed for the carbonyl hydrogen of **1** for reasons given later in this paper.

As indicated in Figure 2C, compound **3** exhibits a single emission line at 0.90 ppm. Based on the multiplicity of this resonance and the chemical shift, we assign this line to ethane. After the irradiation is stopped, the absorption line due to this compound is observed both in the presence and the absence of CCl_4, indicating that this compound is formed in significant amounts. Radical pair ii cannot account for the formation of **3**, unless one postulates that decarbonylation occurs in this radical pair. For this postulate to be valid, the lifetime for decarbonylation must be comparable with the radical pair lifetime Such a short lifetime is unlikely since propionyl chloride is formed in significant quantities, indicating that the radical $CH_3CH_2CO\cdot$ has a sufficiently long lifetime to be trapped by CCl_4. In addition to this information, the polarization for ethane as well as all of the other compounds is quenched when nitric oxide is present in the solution. Furthermore, while ethane is detected after irradiation in the absence of nitric oxide, it is not detected when nitric oxide is present. Since nitric oxide quenches the triplet state of acetaldehyde,[11] these results are consistent with a reaction *via* a radical pair having a triplet pre-

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[10] The g factor and the hyperfine coupling constant are assumed to be the same as the values for the acetyl radical. While there is some uncertainty concerning the magnitude for the hyperfine coupling constant, the range of values suggested would not alter our conclusions; see J. E. Bennet and B. Mile, *Trans. Faraday Soc.*, **67**, 1587 (1971).

[11] C. S. Parmenter and W. A. Noyes, *J. Amer. Chem. Soc.*, **85**, 416 (1963).

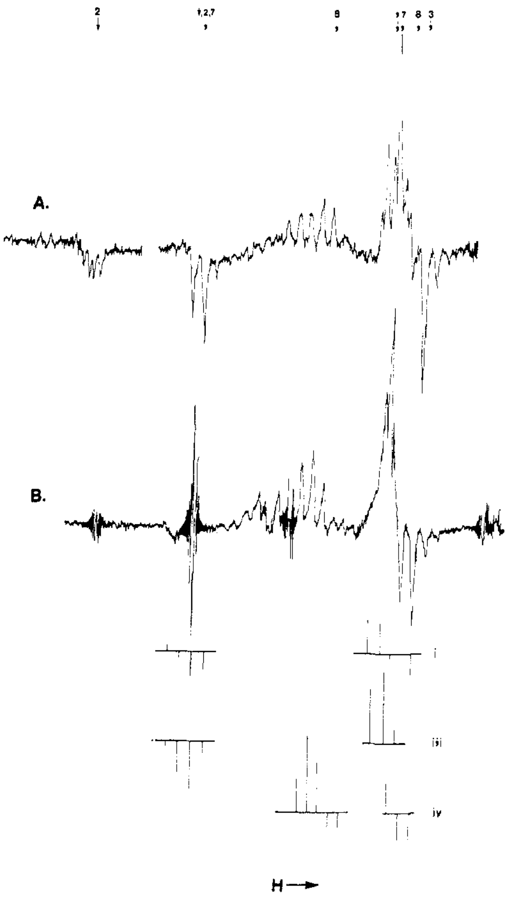

Figure 3. (A) Part of the higher field nmr spectrum obtained at a 500-Hz sweepwidth during irradiation of 0.2 *M* propionaldehyde in perfluoromethylcyclohexane. (B) Same as A except the methyl quartet is spin decoupled. The calculated spectra based on radical pairs i, iii, and iv are given as stick figures at the bottom.

cursor. Consequently, we suggest the following mechanism to explain the polarization observed for **3** in the presence of CCl_4.

$$\mathrm{CH_3CH_2COH^T} \longrightarrow \underset{\mathrm{i}}{[\mathrm{CH_3CH_2\cdot\,\cdot COH}]^T}$$

$$\underset{\mathrm{i}}{[\mathrm{CH_3CH_2\cdot\,\cdot COH}]^T} - \left[\begin{array}{l} \longrightarrow \underset{\mathbf{3}}{\mathrm{CH_3CH_3}} + \mathrm{CO} \\ \longrightarrow \underset{\mathbf{1}}{\mathrm{CH_3CH_2COH}} \\ \longrightarrow \mathrm{CH_3CH_2\cdot} + \mathrm{\cdot COH} \end{array}\right. \qquad (7)$$

According to this mechanism, propionaldehyde in an excited electronic triplet state undergoes α cleavage to give radical pair i which can undergo disproportionation to give **3**, recombination to give **1**, or dissociation to give free radicals. In agreement with experiment, the polarization calculated for **3** according to this mechanism results in emission for ethane. For this calculation, the following values were used: for $\cdot$COH, 2.0009 for g, and $+137$ for A_α;[12] for $CH_3CH_2\cdot$, 2.0026 for g, -22.4 G for A_α, and $+26.9$ G for A_β.[13]

As indicated in eq 2, **1** should also be formed from i; however, no polarization is observed for the CH_3 hydrogens of **1**; *i.e.*, the intensity of the CH_3 hydrogen resonance does not change significantly when the irradiation is stopped. Consequently, i appears to favor dissociation or disproportionation to form **3** to a larger extent than recombination to form **1**. The calculated intensities for the methyl and methylene hydrogens of **1** are illustrated as stick figures in Figure 3. For the carbonyl hydrogen, this calculation predicts emission, but enhanced absorption is observed. Thus, i cannot account for the polarization observed for the carbonyl hydrogen. We will return to this hydrogen later in the paper.

Additional evidence that α cleavage occurs for propionaldehyde comes from the observation of the resonance line for trichloroacetaldehyde (**4**) at 8.95 ppm in Figure 2C. The emission line observed for this compound can be explained by formation *via* the radical pair $[Cl_3C\cdot\,\cdot COH]^F$. The formyl radical comes from dissociation of i and $\cdot CCl_3$ comes from reactions such as

$$\mathrm{CCl_4 + CH_3CH_2CO\cdot \longrightarrow \cdot CCl_3 + CH_3CH_2COCl}$$

which will be discussed below. The disproportionation of this radical pair can also account for the observed emission line for $CHCl_3$ (**5**) at 7.21 ppm. However, it does not seem unreasonable that **5** may be formed from other radical pairs involving $\cdot CCl_3$ with $CH_3CH_2\cdot$ and $CH_3CH_2CHOH\cdot$, also.

In addition to the compounds already discussed, propionyl chloride (**6**) is formed in sufficient amounts to permit the observation of its resonance lines after irradiation. Its hydrogens do not appear to be polarized significantly. The following chain mechanism can explain the formation of propionyl chloride without nuclear spin polarization.

$$\mathrm{CH_3CH_2COH + \cdot CCl_3 \longrightarrow CH_3CH_2CO\cdot + CHCl_3}$$

$$\mathrm{CH_3CH_2CO\cdot + CCl_4 \longrightarrow CH_3CH_2COCl + \cdot CCl_3}$$

This mechanism is identical with the one proposed for the reaction of isovaleraldehyde with carbon tetrachloride.[14] Another compound which appears to be formed is ethyl chloride whose methyl hydrogens resonate at 1.54 ppm. Unfortunately, other lines appear to be superimposed. Therefore, we have not presented the calculated spectrum for ethyl chloride. The lines due to this compound are not observed after irradiation is stopped.

In Figure 2A, the spectra due to **1**, **2**, and **3** are observed in addition to several other compounds which must be formed *via* radical pairs formed from free radicals. This conclusion is based on the fact that these compounds are not observed when CCl_4 is present in the solution. We have been able to identify 3-pentanone (**7**) and 3-pentanol (**8**) by adding them to the solution. As indicated in Table I, the methylene hydrogen resonance for **7** occurs at about the same frequency as the methylene hydrogen resonance for **1**, whereas the methyl hydrogens can be observed separately for each compound. This can be seen in Figure 3A which illustrates the higher field portion of Figure 2A on an expanded scale. Proof that the quartet at 2.30 ppm is due at least to the methylene hydrogens of **1** and **7** is obtained when the quartet at 2.30 ppm is saturated (Figure 3B). As can be seen, each triplet at 1.10 ppm has collapsed to a single line, indicating

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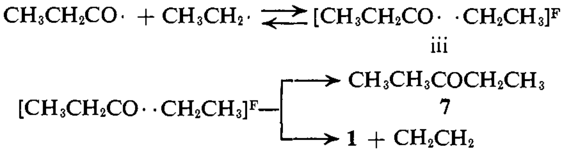
[12] F. Adrian, E. Cochran, and V. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

[13] The signs of the hyperfine constants are taken from ref 6.

[14] S. Winstein and F. Seubold, *J. Amer. Chem. Soc.*, **69**, 2916 (1947).

that the quartet at 2.30 ppm is due to the methylene hydrogens of at least two different compounds. It should be pointed out that the 2-methylene hydrogens of **2** resonate at 2.30 ppm, also. However, as pointed out above, the methyl hydrogens to which these methylene hydrogens are coupled are not polarized in radical pair ii and, therefore, the resonance is not observed. Thus, the triplet at 1.07 ppm cannot be due to the 1-methyl hydrogens of **2**. Additional support for this conclusion is the fact that this triplet disappears when CCl_4 is present (see Figure 2C). Since CCl_4 should not interfere in the formation of radical pair ii, the triplet at 1.07 ppm should not disappear if it is due to a methyl group of **2**. Thus, it seems likely that **7** is formed during the photolysis of **1**.

Since the CCl_4 experiments indicate that **7** is formed from free radicals, we propose the following mechanism. In this mechanism, the superscript F indicates that iii is formed from free radicals.

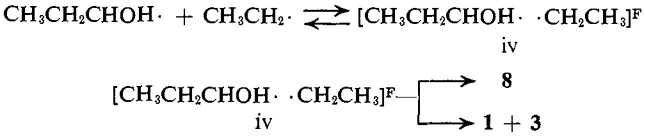


$$\mathrm{CH_3CH_2CO\cdot + CH_3CH_2\cdot \rightleftarrows \underset{iii}{[CH_3CH_2CO\cdot\ \cdot CH_2CH_3]^F}}$$

$$\mathrm{[CH_3CH_2CO\cdot\cdot CH_2CH_3]^F}\begin{cases}\longrightarrow \underset{\mathbf{7}}{\mathrm{CH_3CH_3COCH_2CH_3}}\\ \longrightarrow \mathbf{1} + \mathrm{CH_2CH_2}\end{cases}$$

The calculated spectrum for **7** based on radical pair iii is illustrated as stick figures in Figure 3. In addition to combination, we have indicated the possibility that iii might undergo a disproportionation reaction, although we have no evidence for this step. Although this step would result in enhanced absorption for the carbonyl hydrogen of **1**, it cannot account for the observed enhanced absorption in the presence of CCl_4. Therefore, we have ruled out this step as an explanation for the enhanced absorption of the carbonyl hydrogen of **1**.

Returning to Figure 3B, note that when the two triplets are collapsed by decoupling, a new emission line at 0.97 ppm can be observed. We assign this line as the central line of the triplet for the methyl hydrogens of 3-pentanol (**8**). The upfield line of this triplet superimposes the line for ethane. The methylene-hydrogen resonance for this compound appears as a quintet at 1.42 ppm. The results of decoupling experiments are consistent with this assignment. Some weak lines at about 3.50 ppm appear to be due to the methine hydrogen. We suggest the following mechanism to account for the formation of **8**. In addition to combination in radical pair iv to give **8**, we have indicated the possibility of disproportionation to give **1** and **3**.



$$\mathrm{CH_3CH_2CHOH\cdot + CH_3CH_2\cdot \rightleftarrows \underset{iv}{[CH_3CH_2CHOH\cdot\ \cdot CH_2CH_3]^F}}$$

$$\underset{iv}{\mathrm{[CH_3CH_2CHOH\cdot\ \cdot CH_2CH_3]^F}}\begin{cases}\longrightarrow \mathbf{8}\\ \longrightarrow \mathbf{1} + \mathbf{3}\end{cases}$$

While this step is a possibility, we have no evidence for it. Furthermore, this step cannot account for the formation of **3** when CCl_4 is present, since one would not expect radical pair iv to form in the presence of CCl_4. Thus the formation of **3** in part *via* radical pair i seems likely. The calculated relative line intensities for the methine hydrogen lines have been omitted since the observed resonance lacks sufficient detail for comparison.

Thus, it is possible to account for most of the lines in Figure 2A in terms of two primary photochemical steps for propionaldehyde in perfluoromethylcyclohexane, one involving α cleavage, eq 7, and the other involving hydrogen abstraction, eq 5, both processes occurring *via* an excited triplet state. In contrast, CIDNP from the photochemistry of acetaldehyde appears to result mainly from hydrogen abstraction.[1] The trend toward α cleavage in going from acetaldehyde to propionaldehyde to pivalaldehyde[2] corresponds with the relative stabilities of the methyl, ethyl, and *tert*-butyl radicals.[15]

In our analysis of Figure 2A, we have made no attempt to identify the several compounds which give rise to the broad featureless region around 1.60 ppm, since any assignment would be inconclusive. At any rate, the identification of these compounds would not alter our conclusion that α cleavage and hydrogen abstraction are photolytic paths for propionaldehyde in perfluoromethylcyclohexane.

As indicated above, none of the proposed radical pairs can account completely for the enhanced absorption observed for the carbonyl hydrogen of **1**. Although a reaction analogous to eq 6 may account for part of the enhancement, it cannot account for all of it, since much of the enhancement is still observed during the irradiation of propionaldehyde-*2,2-d*$_2$. Furthermore, using NO as a triplet quencher[16] seems to rule out the possibility that the enhancement occurs by way of a radical pair which has a singlet precursor. In the presence of NO, no polarization is observed. Closs and Paulson[17] have proposed the following mechanism to account for the enhanced absorption observed for the carbonyl hydrogen of benzaldehyde during irradiation in solution.

$$\mathrm{[RCHOH\cdot\cdot OCR]^T \longrightarrow {}^*R\dot{C}HOH + {}^*\dot{R}CO}$$
$$\mathrm{{}^*R\dot{C}HOH + RCOH \longrightarrow {}^*RCOH + R\dot{C}HOH}$$

The asterisk indicates nuclear spin polarization. Our results for propionaldehyde-*2,2-d*$_2$ are consistent with this mechanism. Since the radical pair proposed in this mechanism is identical with the one given in eq 5, it is also consistent with this equation. The enhanced absorption observed for the aldehyde proton in the presence of CCl_4 is consistent with this mechanism if the hydrogen atom transfer occurs more rapidly than CCl_4 trapping[18] or if the compound *RCHOHCl which results from trapping converts to aldehyde and HCl faster than the spin–lattice relaxation rate for its protons.

Finally, as can be seen in Figure 2A, there is a weak emission at 9.61 ppm. We have not made an assignment for this line at the present time. In addition, if the solution is irradiated continuously, the carbonyl hydrogen resonance of **1** gradually undergoes a change from enhanced absorption to emission over a period of about 5 min. We suspect that the change is due to a build-up of product which in turn reacts photochemically to give **1**.

In conclusion, the esr and CIDNP results are consistent with the occurrence of two primary photochemical processes *via* an excited electronic triplet state during

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(15) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

(16) Nitric oxide was chosen since it quenches the triplet state of acetaldehyde; see ref 11.

(17) G. Closs and D. Paulson, *J. Amer. Chem. Soc.*, **92**, 7229 (1970).

(18) The rate constant deduced for this transfer in ref 17 seems large enough for this possibility.

irradiation of propionaldehyde in perfluoromethylcyclohexane: α cleavage; and hydrogen abstraction from a ground state aldehyde molecule. The relative importance of these processes cannot be determined conclusively from our results.

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Photoionization Mass Spectrometer Studies of Gas Phase Ozone–Olefin Reactions

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Abstract: The room temperature gas phase reactions of ethylene, *cis*-2-butene, and isobutene with ozone at pressures of *ca.* 2 Torr have been investigated using photoionization mass spectrometry. Both radical species and stable products were identified and were followed as a function of time. The implications of these observations to the mechanism of gas phase ozone–olefin reactions are discussed.

This investigation of the intermediates and products of the reaction of selected oleffns (ethylene, *cis*-2-butene, and isobutene) with ozone using photoionization mass spectrometry was undertaken as part of a larger study dealing with the chemiluminescence observed in these reactions and its relationship to the overall reaction mechanism. Previous room temperature studies of the chemiluminescence at approximately 2 Torr total pressure, to be reported in more detail later, have identified the emitting species common to all three reactions as electronically excited formaldehyde($^1A''$) and OH($A^2\Sigma^+$) as well as the Meinel band emission from vibrationally excited OH radicals.[1–5] The similarity of the OH Meinel band emission to that from the well-known reaction[6–8]

$$H + O_3 \longrightarrow OH_{\nu}{}^{\dagger}{}_{\leq 9} + O_2$$

suggests the presence of H atoms in these reactions. In the *cis*-2-butene reaction a fourth emission at 520 nm has been tentatively identified as glyoxal phosphorescence ($^3A_u \rightarrow {}^1A_g$).

While much excellent work on the overall kinetics, final products, and mechanisms of gas phase ozone–olefin reactions has been done over a wide range of reactant concentrations,[9–18] the intermediates, and hence the detailed mechanisms, remain obscure. For example, the Criegee mechanism of ozonolysis, which has been established to be a major reaction pathway in the liquid phase,[19] has generally been applied to the gas phase reactions. Thus, the formation of a number of the observed stable products can be rationalized in terms of the decomposition and reactions of the Criegee "zwitterion" (or biradical in the gas phase). However, direct evidence for its existence in the gas phase is lacking, as indeed it is in the liquid phase. In addition, the anomalous effects of reactant concentration on the experimentally determined rate constants[11–13, 15–17] remain unexplained.

Ozone–olefin reactions are known to be involved in the formation of photochemical smog. However, because of the paucity of data on the intermediates and mechanisms of these reactions, little is known about the detailed interaction of these intermediates and products with other atmospheric constituents.[20] While these reactions have been postulated to act as a source of chain carrying OH radicals,[20] it is only recently that any evidence for their production from low pressure ozone–olefin reactions has been obtained.[1] Thus, the elucidation of these reaction mechanisms is of importance to both fundamental and applied chemistry.

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