

# Photochemistry of Acetone in Liquid Phase Studied by CIDNP

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**Abstract:** The photolysis of acetone has been studied in D<sub>2</sub>O and CD<sub>3</sub>CN–D<sub>2</sub>O mixtures by means of nmr spectroscopy. During irradiation, enhanced absorption and emission lines are observed for an acetone and a number of photoproducts. By analysis of the relative intensities of these lines according to the radical pair model for CIDNP, it is possible to conclude that acetone reacts *via* its excited state triplet, and it is possible to indicate mechanisms by which many of the products are formed. Additional information about the details of these reactions was obtained by studying the photolysis of acetone in the presence of CCl<sub>4</sub>, which acts as a radical scavenger, and in the presence of isopropyl alcohol. In the case of the second compound the studies include isopropyl alcohol-*h*<sub>8</sub> plus acetone-*h*<sub>6</sub>, isopropyl alcohol-*h*<sub>3</sub> plus acetone-*d*<sub>6</sub> and isopropyl alcohol-*d*<sub>3</sub> plus acetone-*h*<sub>6</sub>.

The photolysis of acetone in liquid phase has been the subject of various investigations using product determination<sup>1,2</sup> and the detection of intermediates by optical<sup>3</sup> and esr<sup>4</sup> spectroscopy. Since chemically induced dynamic nuclear spin polarization (CIDNP) can provide information not available to these techniques, we wish to report the results of our study of the photolysis of acetone using the CIDNP technique. With this technique, we have obtained evidence for a variety of primary and secondary steps of which a number have been detected in the vapor phase but only a few in the liquid phase photolysis of acetone.<sup>1,3,4</sup> In addition, our results indicate some details not detected previously. Finally, because the CIDNP technique provides information about reactions involving radical pairs, our results do not rule out the possibility of other steps.

## Experimental Section

**Chemicals.** Acetone (Baker Chemical Co.), isopropyl alcohol (Baker Chemical Co.), and carbon tetrachloride (Matheson Coleman and Bell) were distilled and checked by glc and nmr spectroscopy. Deuterioacetonitrile (Merck), deuterioacetone (Merck), D<sub>2</sub>O (Merck), 2-butanone (Aldrich), 3-hydroxy-3-methyl-2-butanone (Aldrich), acetaldehyde (Baker), 1,1,1-trichloroethane (Matheson Coleman and Bell), methyl chloride (Baker), chloroacetone (Eastman Kodak), chloroform (Matheson Coleman and Bell), and *tert*-butyl alcohol (Matheson Coleman and Bell) were used without further purification.

**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.<sup>5</sup> The nmr spectra were obtained before, during, and after irradiation. The radiation source was a 1000 W Hanovia mercury-xenon lamp. No filtering was employed. When a filter was employed to allow transmission of radiation having wavelengths greater than 310 nm, no CIDNP was observed.

## Results and Discussion

During irradiation of various solutions of acetone, transient nmr spectra are obtained. These spectra con-

sist 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.<sup>6</sup>

Details of the theory used to calculate the nuclear spin polarization based on this model have been given previously,<sup>7</sup> 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  $\rho_{ss}$ , which is the diagonal density matrix element for the singlet spin state of the radical pair, is given by the expression

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

In this equation,  $\alpha_{ss}$  and  $\alpha_{TT}$  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 1,  $\gamma = k_1/k_{-2}$ , where *k*<sub>1</sub> is the rate constant for product formation from the radical pair and *k*<sub>-2</sub> is the rate constant for dissociation of the radical pair.  $\mu_j$  is given by the expression

$$\mu_j = \frac{H_{ST}^2/k_{-2}^2}{(1 + \gamma/2)^2 + 4J^2/k_{-2}^2 + (2 + \gamma)H_{ST}^2/k_{-2}^2} \quad (2)$$

In equation 2, *J* is the electron exchange integral, and *H*<sub>ST</sub> 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

$$H_{ST} = \frac{1}{2}\beta H_0(g_1 - g_2) + \frac{1}{2} \sum_I (A_1^I - A_2^I) \times \langle M_I | I_z^I | M_I \rangle \quad (3)$$

In this expression  $\beta$  is the electron Bohr magneton, *H*<sub>0</sub> is the strength of the external magnetic field, *g* is the isotropic electronic *g* factor, *A* is the electron-nuclear coupling constant, *M*<sub>*I*</sub> is the nuclear spin state, *I*<sub>*z*</sub> is the

(1) For a review see T. Berces, "Comprehensive Chemical Kinetics," Vol. 5, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, London, 1972.

(2) (a) I. Taha and R. Kuntz, *J. Phys. Chem.*, **73**, 4406 (1969); (b) N. C. Yang, W. Eisenhardt, and J. Libman, *J. Amer. Chem. Soc.*, **94**, 4030 (1972).

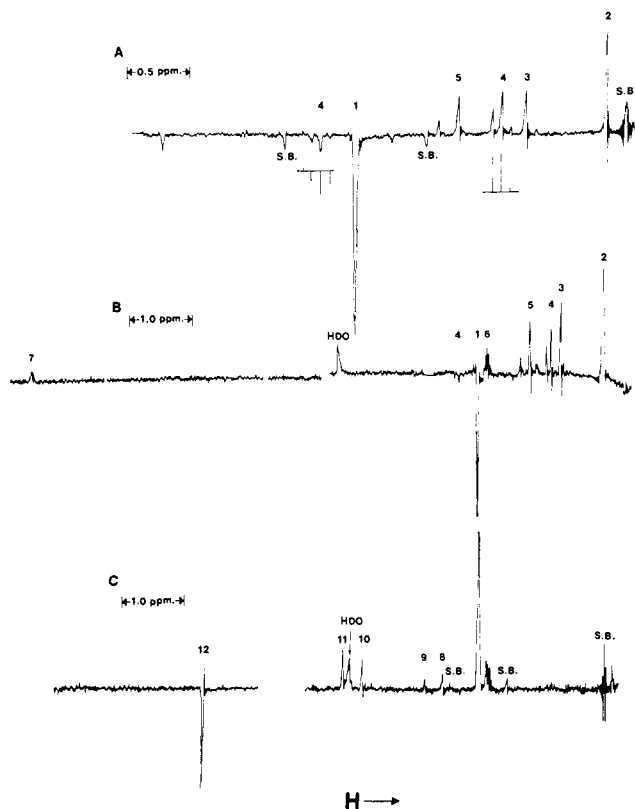
(3) M. Nakashima and E. Hayon, *J. Phys. Chem.*, **75**, 1910 (1971).

(4) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **45**, 1946 (1966).

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

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

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



**Figure 1.** Proton 100-MHz nmr spectra obtained during irradiation using the full spectrum of a 1000-W Hanovia mercury-xenon lamp. The numbers correspond to assignments given in Table I. A. Spectrum of an air-saturated  $D_2O$  solution containing 0.27  $M$  acetone obtained at a 500-MHz sweep width. The emission line due to **1** is off scale. Side bands are indicated by "S.B." Signals not assigned numbers have not been identified conclusively. The stick figures below the spectrum due to **4** are calculated relative intensities based on the radical pair theory given in the text. B. Spectrum of an air-saturated mixture of  $D_2O$ - $CD_3CN$  (1:1 by volume) containing 0.25  $M$  acetone obtained at a 1000-Hz sweep width. With the exception of HDO and  $CHD_2CN$ , **6**, all the signals indicate non-Boltzmann nuclear spin polarization. C. Spectrum of an air-saturated mixture of  $D_2O$ - $CD_3CN$  (1:1 by volume) containing 0.25  $M$  acetone plus 0.1  $M$   $CCl_4$  obtained at a 1000-Hz sweep width. The signal due to **1** is slightly off scale at this gain.

$z$  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  $\gamma$  are  $10^8$  Hz,  $10^9$  sec $^{-1}$ , and 0.2, respectively, and although they are reasonable,<sup>7</sup> 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 acetone.

**Acetone in  $D_2O$  and  $D_2O$ - $CD_3CN$  Mixtures.** The nmr spectrum obtained during the irradiation of an air-saturated solution of 0.27  $M$  acetone in  $D_2O$  is shown in Figure 1A. This spectrum was obtained using the full spectrum of a 1000-W mercury-xenon lamp. 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 TMS side band (labeled "S.B." at high field), all of the lines exhibit either enhanced absorption or emission, indicating non-Boltz-

mann nuclear spin polarization. The assignment of these lines is indicated in Table I. Except for methane

**Table I.** Assignment of Nmr Lines Observed during Irradiation of Acetone in  $D_2O$  or  $D_2O$ - $CD_3CN$  (1:1 by Volume)

Resonance	Position <sup>a</sup>	CIDNP <sup>b</sup>	Compd
<b>1</b>	2.25 s	E	$CH_3COCH_3$
<b>2</b>	0.23 s	A	$CH_4$
<b>3</b>	0.87 s	A	$CH_3CH_3$
<b>4</b>	1.06 t	A (A/E)	$CH_3COCH_2CH_3$
	2.54 q	E (A/E)	$CH_3COCH_2CH_3$
<b>5</b>	1.42 s	A	$(CH_3)_2COHCOCH_3$
	2.33 s	E <sup>c</sup>	$(CH_3)_2COHCOCH_3$
<b>6</b>	2.06 q <sup>d</sup>		$CHD_2CN$
<b>7</b>	9.64 q	A <sup>e</sup>	$CH_3COH$
<b>8</b> <sup>f</sup>	2.80 s	A	$CCl_3CH_3$
<b>9</b> <sup>f</sup>	3.08 s	A	$CH_3Cl$
<b>10</b> <sup>f</sup>	4.18 s	A	$CCl_3CH_2COCH_3$ <sup>g</sup>
<b>11</b> <sup>f</sup>	4.45 s	A	$CH_3COCH_2Cl$
<b>12</b> <sup>f</sup>	7.70 s	E	$CHCl_3$

<sup>a</sup> In ppm relative to TMS; singlet s, triplet t, and quartet q. <sup>b</sup> Absorption A, emission E, and multiplet A/E with A at lower field. <sup>c</sup> Observed when isopropyl alcohol is present; see Figure 2. <sup>d</sup> Quintet. <sup>e</sup> Intensity is larger in  $CD_3CN$ - $D_2O$  than in  $D_2O$ . <sup>f</sup> Observed when  $CCl_4$  is present, Figure 1C. <sup>g</sup> Not confirmed.

and ethane which were assigned on the basis of literature values,<sup>8</sup> the assignments were confirmed by measuring the spectrum for each compound. The unlabeled emission line at lowest field in Figure 1A has not been identified. This line has about the same chemical shift as the methylene hydrogen of acetylacetone observed in  $CCl_4$  solvent. However, since this hydrogen exchanges readily in  $D_2O$ , we cannot rule out the possibility that the line in Figure 1A is due to a different compound. Two other lines (one in absorption and the other in emission) occurring between the lines labeled **1** and **5** have not been assigned. When irradiation is stopped, only the absorption line due to acetone, **1**, is observed.

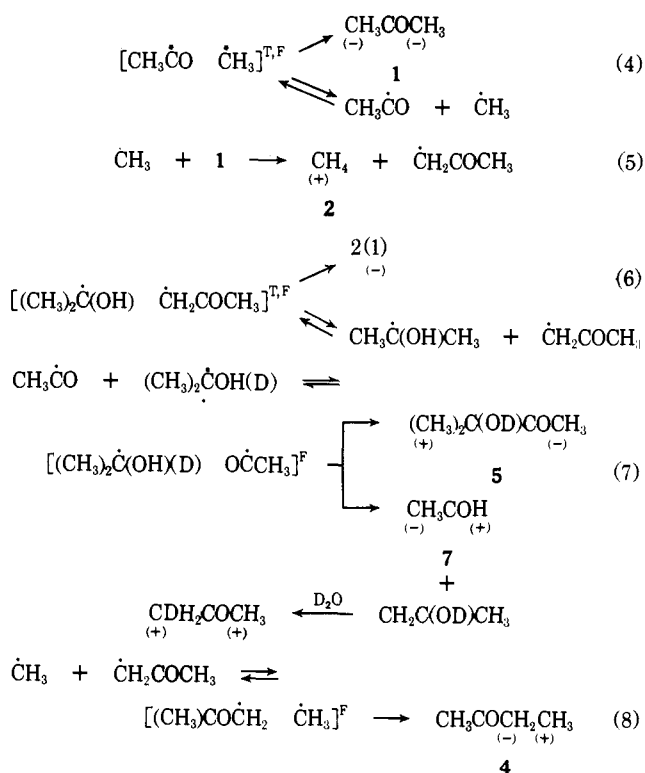
With the exception of the ethane line, it is possible to explain the spectrum illustrated in Figure 1A in terms of the radical pair model and the mechanism given in Scheme I. In this scheme, the brackets indicate a radical pair, and the superscripts indicate that the radical pair has a triplet precursor T and/or free radical precursor F. The D indicates the possibility of deuterium exchange of OH in  $D_2O$ . The signs beneath the products indicate the calculated signs for the nmr signals for the proton: plus for enhanced absorption and minus for emissions. Comparison of the observed signs in Table I with the calculated signs for **2**, **4**, **5**, and **7** indicates that this scheme is consistent with observation. For these calculations, the following values for the isotropic  $g$  factors and the electron-nuclear hyperfine coupling constants were used:  $CH_3\dot{C}O$ , 2.0005, +5.1 G ( $A_\beta$ );<sup>9</sup>  $\dot{C}H_3$ , 2.00252, -22.8 G;<sup>10</sup>  $CH_3CO\dot{C}H_2$ , 2.0044, -19.8 G ( $A_\alpha$ );<sup>4</sup> and  $(CH_3)_2\dot{C}OH$ , 2.0032, +19.7 G ( $A_{CH_3}$ ), +0.54 G ( $A_{OH}$ ).<sup>4</sup> For products containing vicinal protons, a positive value was used for the

(8) L. Jackman and S. Sternhell, "International Series of Monographs in Organic Chemistry," 2nd ed, Vol. 5, D. Barton, and W. Doering, Ed., Pergamon Press, London, 1969, p 164.

(9) J. E. Bennet and B. Mile, *Trans. Faraday Soc.*, **67**, 1587 (1971).

(10) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

Scheme I



indirect nuclear-nuclear coupling constant.<sup>11</sup> As mentioned above, because some of the parameters used in the calculation are somewhat arbitrary, only the relative values of intensities are meaningful. Consequently, for a compound which exhibits only one nmr line, the calculated relative intensity has not been illustrated in Figure 1A unless a comparison with another line is possible. For this reason, only the calculated intensity pattern for the spectrum of **4** is illustrated as stick figures in Figure 1A. The agreement between the calculated and observed spectrum indicates that the mechanism proposed for the formation of **4** is consistent with our experimental results.

According to Scheme I, acetone **1** may be formed by way of five different radical pairs:  $[\text{CH}_3\dot{\text{C}}\text{O} \quad \dot{\text{C}}\text{H}_3]^{\text{T,F}}$ ,  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH}) \quad \dot{\text{C}}\text{H}_2\text{COCH}_3]^{\text{T,F}}$ , and  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH}) \quad \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$ . As indicated in this scheme in eq 7, only  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH}) \quad \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$  gives the wrong sign for the calculated intensity for the nmr line due to **1**. While Figure 1 offers no support for the formation of **1** by way of eq 7, this step has been included because the results using deuterated compounds, presented below, support it. At any rate, eq 4 and 6 can account for the polarization observed for **1** in Figure 1. According to these steps, acetone is excited by radiation and eventually reacts *via* an excited electronic triplet state. Two paths are available to provide CIDNP: bond cleavage to form  $[\text{CH}_3\dot{\text{C}}\text{O} \quad \dot{\text{C}}\text{H}_3]^{\text{T}}$  and hydrogen abstraction from ground state acetone to form  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH} \quad \dot{\text{C}}\text{H}_2\text{COCH}_3]^{\text{T}}$ . We suggest these paths involve the triplet state rather than an excited singlet state because enhanced absorption rather than emission is calculated for the acetone line when these radical pairs have an excited singlet precursor. On the other hand, the observed emission for acetone is consistent with reaction *via* an

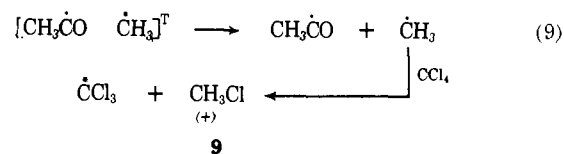
excited singlet state if one postulates that the polarization is determined by radical pairs having free radical precursors. However, this singlet state mechanism is not consistent with the results obtained when  $\text{CCl}_4$  is present as discussed below, and it is not consistent with the polarization observed for methane.

The polarization for methane can be explained by reaction *via* eq 4 and 5. According to this mechanism, the radical pair  $[\text{CH}_3\dot{\text{C}}\text{O} \quad \dot{\text{C}}\text{H}_3]^{\text{T}}$  dissociates to give free radicals whose protons are spin polarized. This polarization is retained in  $\text{CH}_4$  because the methyl radical reacts *via* eq 5 at a rate which is competitive with the nuclear spin relaxation rate for this radical. This mechanism is consistent with the fact that the intensity of the methane signal increases with the increased concentration of acetone. Furthermore, the intensity of this line is increased by the presence of isopropyl alcohol, which is a better hydrogen atom donor. In addition as discussed below, this mechanism is consistent with the enhanced absorption line observed for methyl chloride, **9**, when  $\text{CCl}_4$  is present. A singlet precursor cannot account for these results since emission rather than absorption is calculated for the methane, **2**, line under these conditions. Since the methyl hydrogen resonance of acetaldehyde, **7**, is superimposed on the acetone line, no statement can be made concerning an analogous mechanism for the acetyl radical.

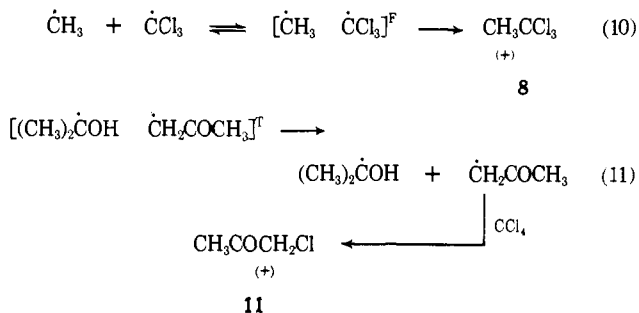
As indicated in Scheme I, free radical precursors as well as the triplet precursor make a contribution to the polarization observed for acetone. In the hope of getting some measure of the relative contribution made by the triplet and free radical precursors, the experiment was repeated in the presence of  $\text{CCl}_4$  which acted as a free radical scavenger. To obtain larger concentrations of  $\text{CCl}_4$  than is possible in  $\text{D}_2\text{O}$ , a mixture of  $\text{D}_2\text{O}$  with  $\text{CD}_3\text{CN}$  (1:1 by volume) was employed. In the absence of  $\text{CCl}_4$ , the irradiation of acetone in this mixture results in a nmr spectrum which is nearly identical with the one for  $\text{D}_2\text{O}$  except that the intensity is lower. This can be seen in Figure 1B which was obtained at twice the sweep width used for Figure 1A.

When 0.1 M  $\text{CCl}_4$  is present in this solution, the spectrum given in Figure 1C is obtained. On comparison of Figure 1C with Figure 1B, one can see that the nmr signals due to **2**, **3**, **4**, and **5** are not detected, and an absorption rather than an emission signal is observed for acetone. In addition, new enhanced signals due to compounds **8**, **9**, **10**, **11**, and **12** are observed. Our assignments are given in Table I. Only the assignment of **10** is unconfirmed since we were unable to obtain this compound.

The absence of signals due to **2**, **4**, and **5** when  $\text{CCl}_4$  is present is consistent with Scheme I since the reaction of  $\text{CCl}_4$  with the free radicals could prevent significant product formation *via* eq 5, 7, and 8. The polarizations observed for **8**, **9**, and **11** are consistent with the formation of these compounds by way of the following steps.



(11) Reference 8, Chapter 4.



Equations 9 and 11 are similar to eq 5 in that the radicals  $\dot{\text{C}}\text{H}_3$  and  $\text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$  are trapped before their nuclei completely lose their polarization. The calculated signs of the polarization are indicated as plus signs beneath the compounds. The agreement with the observed polarization can be seen by referring to Table I. The calculated intensities have not been included in Figure 1 because these intensities cannot be related to each other.

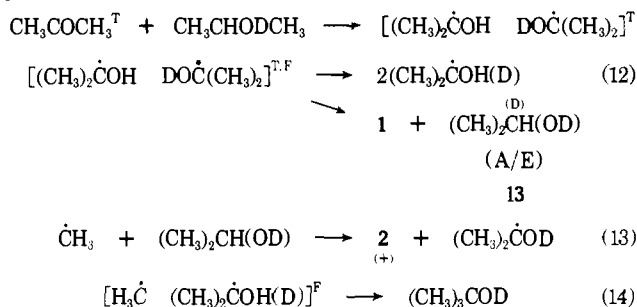
Although an absorption line is observed for acetone during irradiation in the presence of  $\text{CCl}_4$ , the intensity of this line is reduced by about 35% compared with its intensity after irradiation, indicating a negative CIDNP effect as expected for acetone formed from  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH} \dot{\text{C}}\text{H}_2\text{COCH}_3]^{\text{F}}$  and  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH} \dot{\text{C}}\text{H}_2\text{COCH}_3]^{\text{F}}$ . Whether or not this represents the total contribution made to the polarization in Figures 1A and 1B by these radical pairs cannot be decided because other steps may be occurring. For example, it may be possible to trap  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  to form  $(\text{CH}_3)_2\text{C}(\text{OH})\text{Cl}$  which could be a source of positively polarized acetone plus HCl if its decomposition rate is faster than the spin-lattice relaxation rate for its protons. In addition, our results do not indicate the relative importance of  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH} \dot{\text{C}}\text{H}_2\text{COCH}_3]^{\text{F}}$  vs.  $[\text{CH}_3\dot{\text{C}}\text{O} \dot{\text{C}}\text{H}_3]^{\text{F}}$  in photolysis of acetone. However, these results are consistent with Scheme I since they indicate that the polarization observed in the presence of  $\text{CCl}_4$  is determined by both bond cleavage and reduction involving acetone in an excited triplet electronic state.

The emission line observed for  $\text{CHCl}_3$ , **12**, in Figure 1C can be accounted for by reaction by way of the radical pair  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH}) \dot{\text{C}}\text{Cl}_3]^{\text{F}}$ . The details of this reaction will be discussed below.

**Acetone Plus Isopropyl Alcohol.** The photolysis of  $\text{D}_2\text{O}$  solutions containing acetone plus isopropyl alcohol provides additional information about the details of the radical reactions described in the previous section. The nmr spectrum obtained during the irradiation of a  $\text{D}_2\text{O}$  solution containing 0.2 M acetone, **1**, plus 0.2 M isopropyl alcohol, **13**, is illustrated in Figure 2A. In addition to compounds already identified in Table I, polarization is exhibited by isopropyl alcohol, **13** ( $\text{CH}_3$ , doublet, 1.19 ppm; methine, septet, 4.03 ppm), and *tert*-butyl alcohol, **14** ( $\text{CH}_3$ , singlet, 1.26 ppm). The signals at 1.44, 1.83, 2.22, and 4.37 ppm have not been identified conclusively. When isopropyl alcohol is present, the importance of eq 6 in providing measurable nuclear spin polarization is reduced because of competition from an alternate route involving hydrogen abstraction from the alcohol. This conclusion is based on the fact that the intensity of the signals due to **4** is reduced whereas the intensity of the signals due to **5** is increased relative to the methane **2** signal. In fact, in

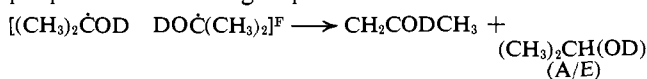
Figure 2A the signals due to **4** are not observed. However, when the sensitivity is increased, the weak  $\text{CH}_3$  resonance of **4** can be detected, as illustrated in Figure 2B. According to an esr study of the photolysis of acetone,<sup>4</sup> the signals due to  $\dot{\text{C}}\text{H}_3$  and  $\dot{\text{C}}\text{H}_2\text{COCH}_3$  are replaced by the signal due to  $(\text{CH}_3)_2\dot{\text{C}}(\text{OH})$  when isopropyl alcohol is present.

A mechanism which can account for the formation of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  observed by esr and in part for the non-Boltzmann polarization illustrated in Figure 2A is given by Scheme I plus the following equations.



As indicated by the esr and nmr results, reaction *via* eq 12 competes favorably with reaction *via* eq 6 to reduce the amount of  $\text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$  radical. According to eq 12, the radical pair  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH} \text{DO}\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$  can give **1** and **13**. A deuterium is indicated in this radical pair since the solvent is  $\text{D}_2\text{O}$  and the OH hydrogen of **13** is expected to be replaced by deuterium. Since this radical pair contains two radicals having identical *g* factors (2.0032), the net polarization calculated for **1** is zero, and this step should not affect the intensity of the signal due to **1**. For this calculation, values of +19.7 G and +0.54 G were used for the hyperfine coupling constants for the  $\text{CH}_3$  and OH proton, respectively. The relative intensity patterns calculated for the methine signals of **13** are illustrated as stick figures in Figure 2. As for **1**, these calculated intensities indicate no net polarization for each type of hydrogen of **13** since the sum of the intensities of the emission and absorption lines is zero. For comparison with the observed polarization, it is necessary to subtract the intensities of the lines measured in the absence of radiation (indicated by the dashed lines) from the intensities given in Figure 2A. In this figure it is possible to compare the methine hydrogen resonance lines with only the emission line of the methyl resonance since the methyl absorption line is off scale. The ratio of these intensities agrees well with the calculated value. Although zero net polarization for the methyl resonance of **13** cannot be ascertained from the spectrum illustrated in Figure 2A, it is verified in Figure 2B which is a spectrum obtained using 0.27 M acetone plus 0.26 M isopropyl alcohol- $d_8$ .

Figure 2B indicates that the disproportionation step given by eq 12 cannot account for all of the polarization observed for **13** because the radical pairs which could form **13** under these conditions would be  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH} \text{DO}\dot{\text{C}}(\text{CD}_3)_2]^{\text{F}}$ ,  $[(\text{CD}_3)_2\dot{\text{C}}\text{OH} \text{DO}\dot{\text{C}}(\text{CD}_3)_2]^{\text{F}}$ , and  $[(\text{CH}_3)_2\dot{\text{C}}\text{OD} \text{DO}\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$ . If the disproportionation occurs as indicated in eq 12, none of these radical pairs could form  $(\text{CH}_3)_2\text{CHOD}$  whose nmr spectrum is indicated in Figure 2B. For this reason we propose the following step.



In addition to the desired alcohol, this disproportionation step gives the enol of acetone which probably converts rapidly (see below) to acetone having zero net polarization. CIDNP evidence for enol formation has been presented for other systems also.<sup>12,12c</sup> The relative intensity pattern calculated for the methine and methyl hydrogens of **13** based on this step is identical with the one calculated for eq 12, although the absolute intensity is much greater than that for eq 12. However, because only one of the four possible radical pairs provides  $(\text{CH}_3)_2\text{CHOD}$ , it is not possible to determine the relative contributions made to the polarization by the two paths. Furthermore, our results give no indication concerning the relative contribution of the two paths to product formation.

For methane, **2**, the trapping step given by eq 13 competes with eq 5, and enhanced absorption is calculated for its nmr resonance. In addition, a disproportionation reaction involving the radical pair in eq 14 could also make a contribution to the positive polarization observed for **2**.

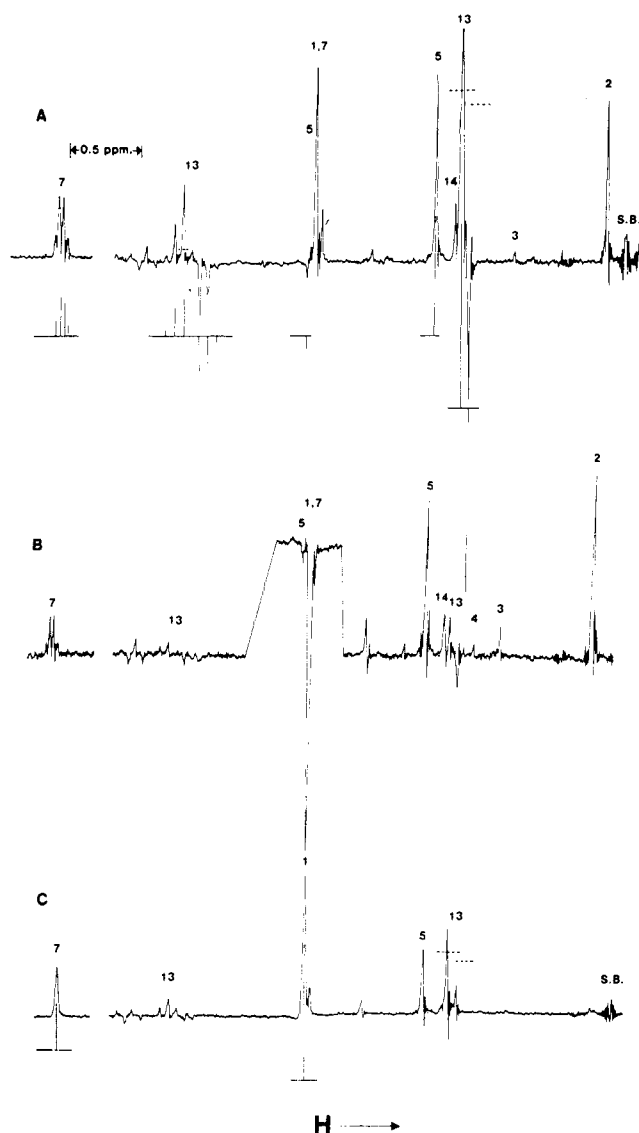
In the presence of isopropyl alcohol, the intensities of the lines due to **5** (Figure 2A) are increased relative to the signals of other compounds, as might be expected for reaction *via* eq 7. The calculated relative intensities based on this step are given as stick figures in Figure 2 to illustrate the agreement with the observed values.

As indicated in eq 7, the radical pair  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH}(\text{D}) \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$  may also undergo disproportionation to form acetaldehyde, **7**, and the enol of acetone which converts to acetone at a rate faster than the spin-lattice relaxation rate for its protons. This conclusion is based on the intensities for the nmr lines of **1** and **7** given in Figures 2B and 2C. Since Figure 2B was obtained using isopropyl alcohol- $d_8$ , the possible radical pairs are  $[(\text{CD}_3)_2\dot{\text{C}}\text{OD} \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$  and  $[(\text{CH}_3)_2\dot{\text{C}}\text{OD} \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$ . Disproportionation involving OD results in  $\text{CH}_3\text{COD}$  which has no signal at 9.64 ppm. Thus, when isopropyl alcohol- $d_8$  is present, the disproportionation must involve enol formation as indicated in eq 7. Additional support for this conclusion is given by the relative intensities of the lines for the carbonyl hydrogen of **7** and the methyl hydrogen of **1** given in Figure 2C. However, before discussing this it is convenient to consider the polarization observed for acetone **1** in Figures 2A–C.

As indicated by Scheme I and subsequent equations, acetone, **1**, may be formed by reaction *via* a variety of radical pairs when isopropyl alcohol, **13**, is present. Under these conditions,  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH}(\text{D}) (\text{D})\text{HO}\dot{\text{C}}(\text{CH}_3)_2]^{\text{T,F}}$ ,  $[\text{CH}_3\dot{\text{C}}\text{O} \dot{\text{C}}\text{H}_3]^{\text{T,F}}$ , and  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH}(\text{D}) \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$  probably account for most of the acetone formation. Of these radical pairs, only  $[\text{CH}_3\dot{\text{C}}\text{O} \cdot \text{CH}_3]^{\text{T,F}}$  and  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH}(\text{D}) \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$  contribute to the polarization observed for acetone. As mentioned above, the calculated polarizations for acetone based on  $[\text{CH}_3\dot{\text{C}}\text{O} \dot{\text{C}}\text{H}_3]^{\text{T,F}}$  and  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH}(\text{D}) \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$  are negative and positive, respectively. Thus, the signal due to **1** in Figure 2A is a superposition of the non-

(12) (a) S. Rosenfeld, R. Lawler, and H. Ward, *J. Amer. Chem. Soc.*, **95**, 946 (1973); (b) B. Blank and H. Fischer, *Helv. Chim. Acta*, **56**, 506 (1973).

(12c) NOTE ADDED IN PROOF. Recently, Fischer has reported detecting the enol during the irradiation of acetone–isopropyl alcohol mixtures. Its spectrum lies in the same region as some of the unidentified lines illustrated in Figure 2. See, G. Laroff and H. Fischer, *Helv. Chim. Acta*, **56**, 2011 (1973).



**Figure 2.** Proton 100-MHz nmr spectra obtained during irradiation using the full spectrum of a 1000-W Hanovia mercury–xenon lamp. A. Spectrum of an air-saturated  $\text{D}_2\text{O}$  solution of 0.20 M acetone plus 0.20 M isopropyl alcohol obtained at a 500-Hz sweep width. In addition to the assignments already given in Table I, isopropyl alcohol, **13**, and *tert*-butyl alcohol, **14**, have been identified. The dashed lines indicate signal heights in the absence of radiation. The stick figures beneath the signals indicate relative intensities based on the radical pair theory given in the text. B. Spectrum of an air-saturated  $\text{D}_2\text{O}$  solution containing 0.27 M acetone and 0.26 M isopropyl alcohol- $d_8$ . C. Spectrum of an air-saturated  $\text{D}_2\text{O}$  solution containing 0.4 M acetone- $d_6$  and 0.2 M isopropyl alcohol. The stick figures indicate calculated relative intensities. The dashed lines indicate the signal height in the absence of radiation.

Boltzmann polarizations derived from these radical pairs and the Boltzmann polarization. In addition, the methyl resonance of acetaldehyde, **7**, occurs at the same position as the acetone signal and contributes negative polarization. Since the intensity of the signal in Figure 2A is about half the intensity in the absence of radiation,  $[\text{CH}_3\dot{\text{C}}\text{O} \dot{\text{C}}\text{H}_3]^{\text{T,F}}$  contributes more polarization than  $[(\text{CH}_3)_2\dot{\text{C}}\text{OH}(\text{D}) \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F}}$  at this concentration of isopropyl alcohol.<sup>13</sup> When the concentration of isopropyl alcohol is lowered to about 0.1 M, emission is

(13) The contribution made by the methyl line of acetaldehyde was determined by normalizing the calculated intensities to the observed carbonyl hydrogen line intensity.

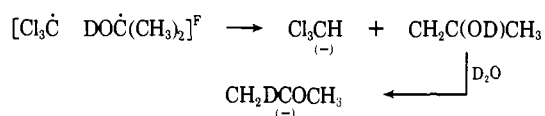
observed for the acetone line. This concentration dependence is consistent with our proposed mechanism. Additional evidence in favor of this mechanism is given in Figures 2B and 2C. Since Figure 2B was obtained using  $\text{CH}_3\text{COCH}_3$  plus 0.26 *M* isopropyl alcohol- $d_8$ , the number of protonated radicals  $(\text{CH}_3)_2\dot{\text{C}}\text{OD}$  produced is reduced to less than one-half the number for a solution containing the same concentration of isopropyl alcohol- $h_8$ .<sup>14</sup> Consequently, the sign of the polarization is determined by  $[\text{CH}_3\dot{\text{C}}\text{O} \ \dot{\text{C}}\text{H}_3]^{\text{T.F.}}$ . On the other hand, Figure 2C was obtained using acetone- $d_6$  and isopropyl alcohol- $h_8$ . Thus,  $[\text{CD}_3\dot{\text{C}}\text{O} \ \dot{\text{C}}\text{D}_3]^{\text{T.F.}}$  makes no contribution, and the observed enhanced absorption is determined by  $[\text{CD}_3\dot{\text{C}}\text{O} \ \text{DO}\dot{\text{C}}(\text{CH}_3)_2]^{\text{F.}}$

This result also provides additional support for the conclusion that eq 7 accounts for the polarization observed for the carbonyl hydrogen of 7. First,  $[\text{CD}_3\dot{\text{C}}\text{O} \ \text{DO}\dot{\text{C}}(\text{CH}_3)_2]^{\text{F.}}$  can provide  $\text{CD}_3\text{COH}$  only by disproportionation to form the enol. Second,  $[\text{CD}_3\dot{\text{C}}\text{O} \ \text{HO}\dot{\text{C}}(\text{CD}_3)_2]^{\text{F.}}$  cannot provide acetone- $h_6$ . Third, the observed relative intensities of the carbonyl hydrogen of 7 and the methyl hydrogen of 1 agree with the values calculated based on eq 7 but do not agree with the values calculated for a disproportionation step involving the hydroxyl hydrogen. The calculated relative intensity pattern for the quartet due to the carbonyl hydrogen of  $\text{CH}_3\text{COH}$ , 7, is illustrated as a stick figure below the signal in Figure 2A to show that the intensity pattern calculated on the basis of eq 7 agrees well with experiment. In addition, the calculation based on eq 7 gives good agreement with experiment for the relative intensities of the single lines due to the carbonyl hydrogen of  $\text{CD}_3\text{COH}$ , 7, and the methyl hydrogen of 1. This can be seen by comparison of the stick figures given below the experimental lines in Figure 2C. The ratio of intensities calculated on the basis of eq 7 for the methyl hydrogen of 1 *vs.* the carbonyl hydrogen is 2.9. In contrast, this ratio is 260 when the carbonyl hydrogen intensity is calculated on the basis of OH hydrogen abstraction. Thus, there is sufficient evidence to conclude that reaction *via* eq 7 occurs. However, these results do not preclude the occurrence of OH hydrogen abstraction, and they give no indication concerning the importance of this process compared with eq 7 in product formation.

In line with these results, emission is observed for the  $\text{CHCl}_3$ , 12, signal during irradiation of a solution containing  $\text{CCl}_4$  and acetone- $h_8$  plus isopropyl alcohol- $d_8$ . Thus, under these conditions, the polarization ob-

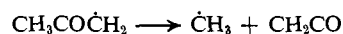
(14) Less than half are produced because this radical can be formed only by eq 8 for the  $d_8$  compound whereas for the  $h_8$  compound it can be formed by eq 8 and 9 and perhaps a trapping step involving  $\text{CH}_3\text{CO}$ .

served for  $\text{CHCl}_3$  is consistent with the following reaction.



Although our results offer evidence in support of three disproportionation steps involving enol formation, it should be emphasized that these results cannot be used to ascertain the extent to which these steps determine product formation.

Because they were unable to detect the esr spectrum of the acetyl radical during irradiation of acetone, Zeldes and Livingston,<sup>4</sup> have suggested that the methyl radical which is detected is formed by the reaction



This possibility is not ruled out; however, it cannot account for our results. Furthermore, our results are not inconsistent with the absence of an esr signal for the acetyl radical since the time scale for our technique appears to be shorter than the time scale for the esr technique. In addition, while biacetyl has been observed as a product resulting from the photodecomposition of acetone,<sup>15a</sup> no net polarization would be observed since  $\Delta g$  is zero for the radical pair  $[\text{CH}_3\dot{\text{C}}\text{O} \ \text{O}\dot{\text{C}}\text{CH}_3]^{\text{F.}}$

Finally, we would like to briefly note the solvent effect on the polarization arising from the irradiation of acetone. We have found that no polarization is observed when the solvent is changed from  $\text{D}_2\text{O}$  to perfluoromethylcyclohexane, deuterioacetonitrile, perdeuteriobenzene, or perfluorobenzene. The reason for this effect is not clear to us. However, a similar increase in the quantum yield for product formation has been observed when the solvent is changed from perfluorodimethylcyclobutane to water.<sup>15b</sup> A more recent study using a variety of solvents<sup>15a</sup> also indicates that the quantum yield for the decomposition of acetone is solvent dependent.<sup>16</sup> A solvent effect on the magnitude of polarization has been noted previously for another system.<sup>17</sup>

**Acknowledgment.** This research has been supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(15) (a) G. Porter, S. Dogra, R. Loutfy, S. Sugamora, and R. Yip, *Trans. Faraday Soc.*, **69**, 1462 (1973); (b) ref 1, p 336.

(16) In addition, no deuterium exchange of acetone was observed when  $\text{CD}_3\text{CN}$  was used as the solvent.

(17) G. Closs and C. Doubleday, *J. Amer. Chem. Soc.*, **94**, 9248 (1972).