

CH₃CN, which is isoelectronic with CH₃CO⁺ and CH₃N₂⁺, is almost certainly <104 kcal/mol.⁴⁸

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References and Notes

- (1) Postdoctoral Fellow, 1974–1975, on leave from Physikalisch Chemisches Institut der Universität, Basel, Switzerland.
- (2) For a brief summary of part of this work, see A. D. Williamson, J. Vogt, and J. L. Beauchamp, *Chem. Phys. Lett.*, **47**, 330 (1977).
- (3) For a review of early work, see J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, **71**, 73 (1971).
- (4) A. H. Laufer and R. A. Keller, *J. Am. Chem. Soc.*, **93**, 61 (1971).
- (5) J. Vogt, M. Jungen, and J. L. Beauchamp, *Chem. Phys. Lett.*, **40**, 500 (1976).
- (6) R. P. Frueholz, W. M. Flicker, and A. Kuppermann, *Chem. Phys. Lett.*, **38**, 57 (1976).
- (7) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964); S.-Y. Ho and W. A. Noyes, *J. Am. Chem. Soc.*, **89**, 5091 (1967); B. A. DeGraff and G. B. Kistiakowsky, *J. Phys. Chem.*, **71**, 3984 (1967); G. B. Kistiakowsky and T. A. Walter, *ibid.*, **72**, 3952 (1968); A. N. Strachan and D. E. Thornton, *Can. J. Chem.*, **46**, 2353 (1968); W. Braun, A. M. Bass, and M. Pilling, *J. Chem. Phys.*, **52**, 5131 (1970); K. Dees, D. W. Setser, and W. G. Clark, *J. Phys. Chem.*, **75**, 2231 (1971); K. Dees and D. W. Setser, *ibid.*, **75**, 2240 (1971); V. Zabransky and R. W. Carr, Jr., *ibid.*, **79**, 1618 (1975).
- (8) D. J. Cram and G. S. Hammond, "Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1964.
- (9) J. E. Del Bene, *J. Am. Chem. Soc.*, **94**, 3713 (1972).
- (10) C. E. Dykstra and H. F. Schaefer III, *J. Am. Chem. Soc.*, **98**, 2689 (1976).
- (11) L. B. Harding and W. A. Goodard III, unpublished work.
- (12) R. L. Nuttall, A. H. Laufer, and M. V. Kilday, *J. Chem. Thermodyn.*, **3**, 167 (1971).
- (13) F. O. Rice and J. Greenberg, *J. Am. Chem. Soc.*, **56**, 2268 (1934).
- (14) For a general review of the technique, see W. A. Chupka in "Ion-Molecule Reactions", J. L. Franklin, Ed., Plenum Press, New York, N.Y., 1972.
- (15) A. C. Hopkinson, *J. Chem. Soc., Perkin Trans. 2*, 795 (1973).
- (16) D. R. Yarkony and H. F. Schaefer III, *J. Chem. Phys.*, **63**, 4317 (1975).
- (17) J. Long and B. Munson, *J. Am. Chem. Soc.*, **95**, 2427 (1973).
- (18) G. A. Olah, K. Dunne, Y. K. Mo, and P. Szilagy, *J. Am. Chem. Soc.*, **94**, 4200 (1974).
- (19) F. P. Boer, *J. Am. Chem. Soc.*, **90**, 6706 (1968).
- (20) J. L. Beauchamp, *Ann. Rev. Phys. Chem.*, **22**, 527 (1971).
- (21) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).
- (22) M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 5781 (1976).
- (23) For a recent application of this instrumentation, see R. H. Staley, J. E. Kleckner, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 2018 (1976).
- (24) For recent applications of this instrumentation in studying ion-molecule reactions, see R. R. Corderman, P. R. LeBreton, S. E. Buttrill, Jr., A. D. Williamson, and J. L. Beauchamp, *J. Chem. Phys.*, **65**, 4929 (1976).
- (25) The preparation follows that given in *Org. Syn.*, **45**, 50 (1965).
- (26) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).
- (27) Data other than those presented in Table II are taken from ref 29. See also, R. W. Taft, "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975.
- (28) Reference data for absolute proton affinities can best fit the relative proton affinities in ref 29 by assuming PA(NH₃) = 202.3 ± 2 kcal/mol (J. L. Beauchamp, R. H. Staley, S. E. Buttrill, J. F. Wolf, and R. W. Taft, unpublished work). See also R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).
- (29) R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 5964 (1977); earlier studies of ΔH_f(CH₃CO⁺) are discussed in this paper.
- (30) Related processes and their implications are discussed by T. B. McMahon and J. L. Beauchamp, *J. Phys. Chem.*, **81**, 593 (1977).
- (31) H. R. Johnson and M. W. Strandberg, *J. Chem. Phys.*, **20**, 687 (1952).
- (32) T. Su and M. T. Bowers, *J. Chem. Phys.*, **58**, 3027 (1973).
- (33) R. Botter, V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, *J. Chem. Phys.*, **45**, 1198 (1966).
- (34) C. B. Moore and G. Pimentel, *J. Chem. Phys.*, **38**, 2816 (1963).
- (35) R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.*, **18**, 118 (1950).
- (36) J. C. Light, *J. Chem. Phys.*, **40**, 3221 (1964); J. C. Light and J. Lin, *ibid.*, **43**, 3209 (1965).
- (37) W. A. Chupka and M. E. Russell, *J. Chem. Phys.*, **49**, 5426 (1968).
- (38) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.
- (39) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).
- (40) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, London, 1972.
- (41) S. A. Safran, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, *Chem. Phys. Lett.*, **12**, 564 (1972).
- (42) A. Lee, R. L. Leroy, F. Herman, R. Wolfgang, and J. C. Tully, *Chem. Phys. Lett.*, **12**, 569 (1972).
- (43) G. F. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).
- (44) A loose complex was assumed in which the vibrational frequencies of ketene appear twice with the addition of five low frequencies to describe the additional modes of the complex. The latter are not critical in the calculation. Frequencies for ketene and ketene-d₂ were taken from ref 34 and W. F. Arendale and W. H. Fletcher, *J. Chem. Phys.*, **26**, 793 (1957). For both cases a frequency of 900 cm⁻¹ was excluded as the reaction coordinate. The parameters in the Whitten-Rabinovitch treatment were E₂ = 1.931 eV and β = 1.410 for the CH₂CO system and E₂ = 1.613 eV and β = 1.341 for CD₂CO.
- (45) R. H. Staley, M. Taagepera, W. G. Henderson, J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 326 (1977).
- (46) M. S. Foster, A. D. Williamson, and J. L. Beauchamp, *Int. J. Mass Spectrom. Ion Phys.*, **15**, 429 (1974).
- (47) A. H. Laufer and H. Okabe, *J. Am. Chem. Soc.*, **93**, 4137 (1971).
- (48) D. J. Bogan and D. W. Setser, *J. Chem. Phys.*, **64**, 586 (1976).

Photoreduction and Photodecarboxylation of Pyruvic Acid. Applications of CIDNP to Mechanistic Photochemistry

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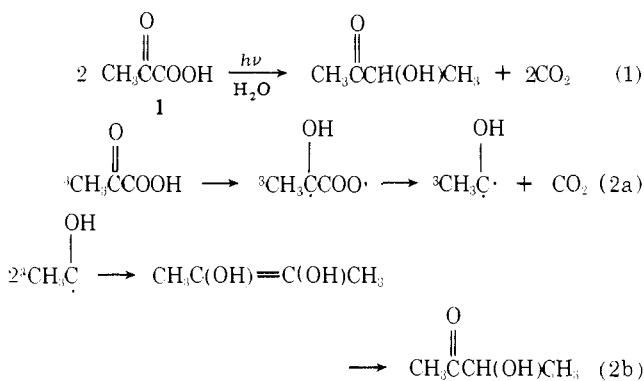
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Abstract: Detailed mechanisms for the reduction of n,π* triplet pyruvic acid by ethanol, 2-propanol, and acetaldehyde in acetonitrile solution have been elucidated by CIDNP. Various geminate combination and disproportionation reactions, including the general formation of pyruvic acid enol (7), are observed. The significance of escape reactions involving hydrogen exchange between ketyl radicals and ground-state pyruvic acid is demonstrated. With moderate concentrations of ethanol, competitive abstraction from product acetaldehyde becomes important. Photodecarboxylation of n,π* triplet pyruvic acid in water and other nonreducing, polar solvents is initiated via unimolecular scission of the carbonyl-carboxy bond. Rapid reduction of ground-state pyruvic acid by carboxyl radicals followed by radical coupling yields 2-hydroxy-2-methylacetoacetic acid (8) as the primary photoproduct in all solvents. The rate coefficient for α-cleavage in acetonitrile solution is estimated to be 1 × 10⁶ s⁻¹. All observations are well explained with the radical pair theory of CIDNP.

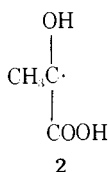
The photophysical and photochemical properties of α-ketocarboxylic acids are not well understood.¹ While it has long been known that irradiation of aqueous solutions of pyruvic acid (1) afford high yields of acetoin (eq 1),² this interesting

transformation has stimulated only coarse mechanistic conjecture (eq 2)³ rationalized by presumed analogy to vapor-phase results.⁴

Pyruvic acid is efficiently photoreduced in the presence of



suitable hydrogen atom donors to yield *meso*- and *dl*-dimethyltartaric acids as the predominant products.^{2c} The reactive state is the n, π^* triplet as deduced from energy transfer quenching experiments⁵ and absorption and emission spectral evidence.^{1b, 2c} Photolytically generated pyruvic acid ketyl radicals (**2**) have been observed directly by electron spin res-



onance spectroscopy,⁶ and kinetic analyses have provided rate coefficients and activation parameters for the abstraction^{5, 6e, h} and termination steps.^{6a, c, f} Despite the detailed nature of these most recent investigations, interpretation of the observed second-order termination rate expression was based on an a priori mechanism describing the fates of the radicals generated during the primary process.^{6f}

The intent of the present research was to provide detailed reaction mechanisms for (1) the photoreduction of pyruvic acid by selected hydrogen donor substrates and (2) the photoinitiated decarboxylation of pyruvic acid in aqueous and other nonreducing environments. The manifold of elementary free-radical reactions comprising both sequences are elucidated by advantageous exploitation of the techniques of chemically induced dynamic nuclear polarization (CIDNP).⁷ The CIDNP probe is uniquely applicable to such investigations in providing direct observation of low yield and/or transient diamagnetic products that would otherwise escape detection. Within the realm of the high-field approximation⁷ the phases of the net and/or multiplet effects observed for a given set of nuclei yield a definitive, yet readily interpretable, description of the reaction sequence affording the specified product. Furthermore, concentration and time dependence studies allow inferences regarding the primary photochemical process.

Experimental Section

All CIDNP and comparative standard spectra were measured with a Bruker HX 90E NMR spectrometer (¹H, 90 MHz; ¹³C, 22.631 MHz) operating in the Fourier transform mode (Nicolet Technology Corp. program NTCFT, version 1002), except as noted otherwise. The deuterated solvent provided an internal lock, and spectral regions were defined by appropriate frequency offsets, thus obviating sample contamination by normal internal references. Reactant concentrations were generally 0.10 (¹H) or 0.50 M (¹³C). The qualitative features of all CIDNP spectra were insensitive to the presence of dissolved oxygen. Reported analytical ¹H NMR spectra were obtained upon a Bruker HS 270 (270 MHz, FT) relative to internal tetramethylsilane. Ultraviolet spectra were measured with a Cary 14 recording spectrophotometer. Mass spectral analyses utilized an AEI MS-9 mass spectrometer interfaced to a PDP 8/1 computer (Digital Equipment Corp.). Data treatment was accomplished with the MSDS II program (Applied Data Research, Inc.).

NMR Optical System. The light source was a 1-kW high-pressure mercury-xenon compact arc (Hanovia 977B-1). The optical train included a 30-mm continuous-flow water filter with quartz windows, an $f/1$ quartz lens, and a 3-mm plate glass filter ($T_{310\text{nm}} = 0.01$). A remote-controlled mechanical shutter could be interposed between the lens and glass filter as desired. The focused light beam was admitted directly into the modified spectrometer probe employing a polished Suprasil light pipe. Steady-state photolysis times were 15 s for ¹H and ca. 10 min (total acquisition time) for ¹³C spectra. All NMR tubes were Pyrex.

Time Dependence Experiments. Constants describing the time evolution of specific polarized signals were determined by a two-pulse sequence phenomenologically represented by $\text{light}(t) - \tau - \pi/2$. The first pulse drove the mechanical shutter, now interfaced with the computer, thus governing the irradiation interval. Variation of this pulse width, coupled with a constant, short delay ($\tau = 0.01$ s), yielded the time constant for generation of a polarized nucleus. Corresponding dynamic T_1 decay values were obtained by fixing the light period (10 s) and altering τ . Comparative static T_1 measurements were made with photolyzed (5 min, sealed tube) mixtures of pyruvic acid and acetaldehyde in acetonitrile-*d*₃ solution by the conventional inversion-recovery ($\pi - \tau - \pi/2$) method. The constants were calculated by χ^2 minimization computer fits of the time-dependent signal intensities to the requisite exponential functions.⁸ All samples were degassed by repeated freeze-pump-thaw cycles to a final pressure of 2×10^{-3} Torr and sealed. All spectra were processed identically.

Concentration Dependence Quenching Experiments. Samples were prepared by diluting various aliquots of naphthalene stock solution (2.01×10^{-2} M) to volume with a given stock solution of pyruvic acid (0.522, 1.00, 2.04×10^{-1} M) in acetonitrile-*d*₃, degassed by repeated freeze-pump-thaw cycles to a final pressure of 2×10^{-3} Torr, and sealed. Variations in impurity quenching were averted by prior mixing of all solvent batches employed. Samples were sequentially irradiated for 15 s with a minimum of 99.9% of the absorbed radiation exciting pyruvic acid. Under the short duration (ca. 30 min) conditions of a given set of experiments, it is assumed that the incident light flux remained effectively constant. All spectra were scaled identically during processing, and integrals were normalized to residual CD₂HCN.

Materials. The following substances were used as obtained: acetaldehyde (Aldrich, 99+%), ethanol (U. S. I., absolute pure), 2-propanol (Mallinckrodt, analytical reagent), acetonitrile-*d*₃ (Aldrich Gold Label, 99 atom % D), benzene-*d*₆ (Stohler, 99.5 atom % D), deuterium oxide (Aldrich Gold Label, 99.8 atom % D), ethanol-*d*₆ (Stohler, anhydrous, 99 atom % D), sulfuric acid-*d*₂ (Stohler, 99 atom % D), and sodium pyruvate-2,3-¹³C₂ (Merck Sharp and Dohme, 90 atom % ¹³C).

The following compounds were synthesized and/or purified as delineated.

Pyruvic Acid. Pyruvic acid (Aldrich Gold Label, 99+%) was rectified under vacuum and stored at -25°C : bp 43°C (2 Torr); UV (CH_3CN) λ_{max} 337 nm (ϵ 16.9 M⁻¹ cm⁻¹); (D_2O) λ_{max} 324 nm.⁹ Samples of ¹³C-labeled pyruvic acid were prepared from aqueous solutions (0.10 M, D_2O) of sodium pyruvate-2,3-¹³C₂ by in situ acidification with sulfuric acid-*d*₂ (3.5 $\mu\text{L}/\text{mL}$).

L(+)-Lactic Acid. L(+)-Lactic acid (Sigma) was twice sublimed immediately prior to use, mp 52.5 – 53.0°C (lit.¹⁰ mp 53°C). Benzene-*d*₆ solutions were saturated (0.028 M) by prolonged sonication.

Naphthalene. Naphthalene (Fisher, certified) was twice recrystallized from ethanol and twice sublimed, UV (CH_3CN) λ_{max} 310 nm (ϵ 240.6 M⁻¹ cm⁻¹).

dl-3-Hydroxy-2-butanone (dl-Acetoin). 2,3-Butanedione was reduced in the presence of granular zinc in aqueous sulfuric acid (10% v/v).¹¹ Following continuous liquid-liquid extraction (ether) and vacuum fractionation, the *dl*-acetoin was purified by preparative GLC¹² (150°C): NMR (CDCl_3) δ 4.27 (q, 1, $J = 7.2$ Hz, $-\text{CHCH}_3$), 3.95 (br, 1, $-\text{OH}$), 2.22 (s, 3, $-\text{COCH}_3$), 1.41 (d, 3, $J = 7.2$ Hz, $-\text{CHCH}_3$).

meso- and dl-Dimethyltartaric Acids. A solution of pyruvic acid (0.28 M) in chloroform was irradiated¹³ for 3 h.^{2c} Crystallization from the reaction mixture and recrystallization from methanol/chloroform (1:1.5 v/v) afforded a mixture of *meso*- and *dl*-dimethyltartaric acids: mp 140 – 158°C (lit.^{2c} mp 140 – 163°C); NMR (CD_3CN) δ 1.48 and 1.44 (2 s, $-\text{CH}_3$).¹⁴

dl-Methyl 2-Hydroxy-2-methylacetoacetate. Pyruvic acid (0.66 g, 7.5 mmol) and acetaldehyde (0.50 g, 11.25 mmol, 1.5 equiv) in

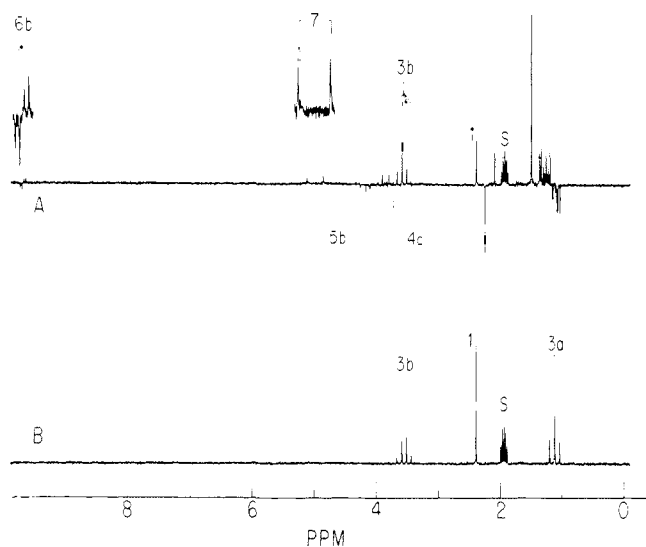


Figure 1. 90-MHz ^1H FT NMR spectra of 0.10 M CH_3COCOOH and 0.10 M $\text{CH}_3\text{CH}_2\text{OH}$ in CD_3CN : (A) during irradiation; (B) following irradiation. Assignments are summarized in Table I; S = solvent.

acetonitrile (75 mL, freshly distilled from P_2O_5 under nitrogen) were irradiated¹³ for 4 h. The subsequent mixture was treated with an excess of ethereal diazomethane,¹⁵ and concentrated in vacuo to yield a viscous, yellow oil (1.06 g). *dl*-Methyl 2-hydroxy-2-methylacetoacetate was isolated and repurified by preparative GLC¹² (190 °C): IR (film)¹⁶ 3460 (OH stretch), 1748 and 1724 cm^{-1} (C=O stretches); NMR (CDCl_3)¹⁶ δ 4.20 (s, 1, -OH), 3.81 (s, 3, -COOCH₃), 2.29 (s, 3, -COCH₃), 1.61 (s, 3, -CH₃); mass spectrum (60 eV) *m/e* (rel intensity, fragment) 104.0477 (20.0, $\text{C}_4\text{H}_8\text{O}_3$), 88.0573 (2.1, $\text{C}_4\text{H}_8\text{O}_2$), 87.0399 (2.1, $\text{C}_4\text{H}_7\text{O}_2$), 42.9509 (100, $\text{C}_2\text{H}_3\text{O}$).

***dl*-Ethyl 2-Hydroxy-2-methylacetoacetate.**¹⁷ Lead tetraacetate (86.9 g, 0.196 mol) was added to a vigorously stirred solution of *dl*-ethyl 2-methylacetoacetate (28.8 g, 0.2 mol, Aldrich, distilled) in benzene (150 mL, freshly distilled from CaH_2) at such a rate (ca. 30 min) that the temperature remained below 30 °C. Following addition, the mixture was gently heated (40 °C) for 5 h, and then allowed to stand at room temperature for an additional 20 h. The mixture was filtered and the cake repeatedly washed with benzene. The benzene solution was thoroughly washed with water, dried (MgSO_4), and concentrated in vacuo. Vacuum fractionation yielded *dl*-ethyl 2-acetoxy-2-methylacetoacetate (10.20 g), bp 75–78 °C (1 Torr). *dl*-Ethyl 2-acetoxy-2-methylacetoacetate (5.05 g, 25 mmol) was added to sodium bicarbonate (4.2 g, 50 mmol) in water (75 mL). After stirring at room temperature overnight, ether extraction gave *dl*-ethyl 2-hydroxy-2-methylacetoacetate (2.35 g, 59%). Purification was effected by preparative GLC¹² (190 °C): mass spectrum (60 eV) *m/e* (rel intensity, fragment) 118.0623 (48.4, $\text{C}_3\text{H}_{10}\text{O}_3$), 90.0319 (36.8, $\text{C}_3\text{H}_6\text{O}_3$), 88.0518 (3.2, $\text{C}_4\text{H}_8\text{O}_2$), 87.0449 (19.7, $\text{C}_4\text{H}_7\text{O}_2$), 42.9501 (100, $\text{C}_2\text{H}_3\text{O}$). Attempts at in situ saponification, followed by acidification to yield stable samples of *dl*-2-hydroxy-2-methylacetoacetic acid^{17,18} were unsuccessful: ^{13}C NMR analyses afforded spectra corresponding to mixtures of *dl*-acetoin and ethanol.

***erythro*- and *threo*-2,3-Dihydroxy-2-methylbutanoic Acids.** Sodium borohydride (0.15 g, 4 mmol) was slowly added to *dl*-ethyl 2-hydroxy-2-methylacetoacetate (0.65 g, 4 mmol) in ethanol (10 mL). After stirring for 1 h, the mixture was hydrolyzed and extracted with ether, and the extract was concentrated in vacuo. The resultant residue was dissolved in water (50 mL) and treated with Amberlite IR-120 resin (1.0 g, 24-h reflux). The resin was separated by filtration and thoroughly rinsed with water. The pale yellow filtrate was concentrated by vacuum distillation to afford a mixture of *erythro*- and *threo*-2,3-dihydroxy-2-methylbutanoic acids:^{16,19} NMR (CD_3CN) δ 3.88 (q, 1, $J = 6.4$ Hz, -CHCH₃), 3.77 (q, 1, $J = 6.4$ Hz, -CHCH₃), 1.34 (s, 3, -CH₃), 1.25 (s, 3, -CH₃), 1.13 (d, 3, $J = 6.4$ Hz, -CHCH₃), 1.11 (d, 3, $J = 6.4$ Hz, -CHCH₃).

α -Methoxyacrylic Acid. Methyl 2,3-dibromopropanoate (12.30 g, 50 mmol) in methanol (15 mL, freshly distilled from magnesium turnings) was added dropwise to a magnetically stirred mixture of sodium methoxide (8.10 g, 150 mmol, 3 equiv) in methanol (40 mL).

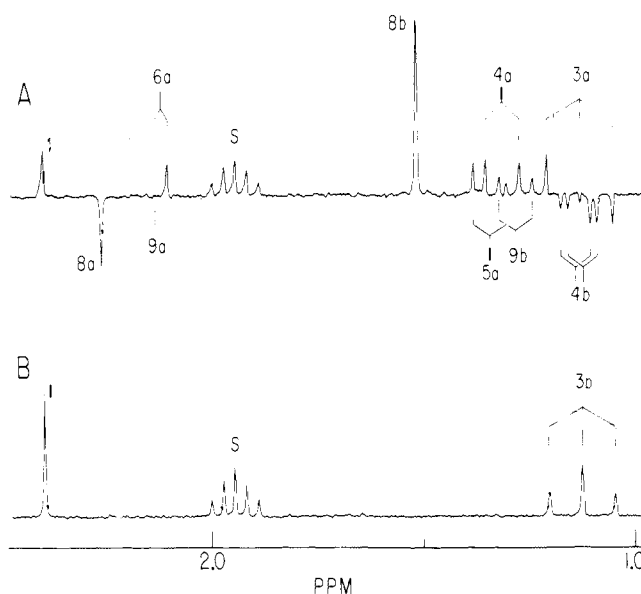


Figure 2. High-field portion of Figure 1: (A) during irradiation; (B) following irradiation. Assignments are summarized in Table I; S = solvent.

The milky white mixture was stirred at room temperature for 10 days under a positive pressure of nitrogen. Dry ice was added to neutralize the excess sodium methoxide. The mixture was filtered into water, and the aqueous phase was extracted with chloroform. Concentration and distillation under hydroquinone under a reduced pressure of nitrogen yielded methyl α -methoxyacrylate.²⁰ The entire distillate was refluxed in aqueous sodium hydroxide (15 mL, 1 N) for 1.5 h. After cooling, the mixture was acidified with aqueous hydrochloric acid (15 mL, 1 N) and extracted with ether. The extract was washed with water, dried (MgSO_4), and concentrated to give a pale yellow liquid (0.67 g). Treatment of the residue with hot hexane (60 mL) and cooling yielded α -methoxyacrylic acid (0.13 g) as white needles: mp 53.5–54.0 °C (lit.²¹ mp 52 °C); NMR (CD_3CN) δ 5.29 and 4.71 (doublets, 2, $J = 2.6$ Hz, =CH₂), 3.62 (s, 3, -OCH₃).

Results and Discussion

Photoreduction of Pyruvic Acid. Figure 1 illustrates the ^1H NMR spectrum obtained during photolysis ($\lambda > 310$ nm) of pyruvic acid (0.10 M) and ethanol (0.10 M) in acetonitrile- d_3 solution. A subsequent dark spectrum is included for comparative purposes. The high-field portion of the spectrum contains the majority of mechanistic information; thus expansions of this region are depicted (Figure 2). The designated spectral assignments (Table I) are based upon spectra of authentic materials and/or appropriate model compounds and isolation and independent characterization of specific products. The magnetization was sampled by a $\pi/6$ pulse to prevent distortions of the multiplet effects.²² Transitions indicated as being absent were readily detected (at the expense of considerable phase distortion) by employing a $\pi/2$ sampling pulse.

Application of the qualitative phase relationships derived from the radical pair theory of CIDNP under conditions of dominant S-T₀ mixing²³ yields the reaction mechanism formulated in eq 3–12. Nuclear spin polarized species are indicated by an asterisk. Table I summarizes the spectral assignments, observed polarization phases, and those phases predicted by the mechanism assuming triplet multiplicity of the precursor and the reaction type, geminate vs. escape, as illustrated. The requisite magnetic parameters of the radicals involved are catalogued in Table II. Signs of the hyperfine coupling constants are taken to be positive and negative for protons β and α , respectively, to the free valence carbon atom. Geminal and vicinal nuclear-nuclear spin coupling constants are as-

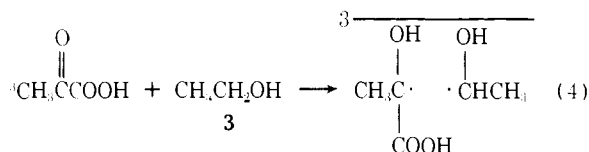
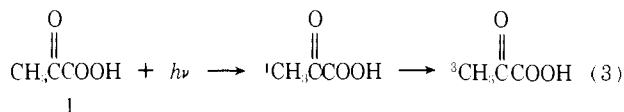
Table I. ^1H NMR Spectral Assignments and Polarization Phases: Pyruvic Acid Plus Ethanol in Acetonitrile- d_3

Spectral assignment ^a	Code no.	Polarization phase	
		Obsd	Predicted (eq)
$\text{CH}_3\text{COCO}^*\text{OH}$	1	E	A (5d, 7c) E (9)
$\text{CH}_3\text{CH}_2^*\text{OH}$	3a	E + AE	E + AE (5c, 5d)
$\text{CH}_3\text{C}^*(\text{OH})\text{CH}^c(\text{OH})\text{CH}_3^b$ COOH	3b	A + AE	A + AE (5c, 5d)
	4a	A	A (5a)
$\text{CH}_3\text{CH}^b(\text{OH})\text{COOH}$	4b	E + AE	E + AE (5a)
	4c	A + AE	A + AE (5a)
	5a	A + AE	A + AE (5b)
$\text{CH}_3\text{CH}^b\text{O}$	5b	E + AE	E + AE (5b)
	6a	A + EA	E + AE (5b) A + EA (8) E (7b, 7c)
$\text{H}_2\text{C}=\text{C}(\text{OH})\text{COOH}$	6b	E + EA	A + AE (5b) E + EA (8) A (7b, 7c)
	7	A + AE	A + AE (5c) A (7b)
$\text{CH}_3\text{COC}(\text{OH})\text{CH}_3^b$ COOH	8a	E	E (7a)
$\text{CH}_3\text{COCH}^c(\text{OH})\text{CH}_3^b$	8b	A	A (7a)
	9a	E	E (12)
	9b	A	A (12)
	9c	E	E (12)

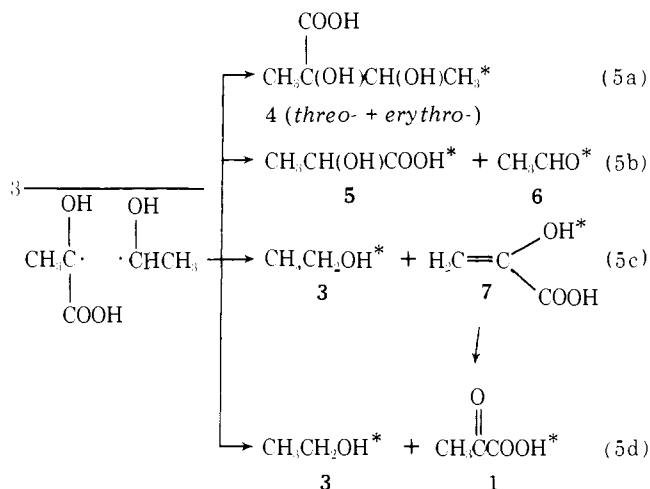
^a Nuclear superscripts refer to code subclassifications.

signed negative and positive values, respectively. Estimated product yields are also indicated.

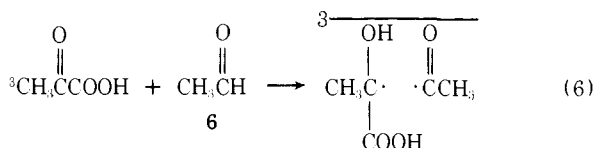
Formation of the first pair



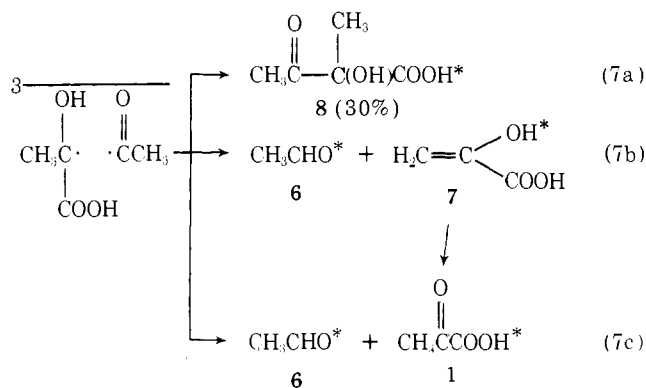
Geminate reactions of the first pair



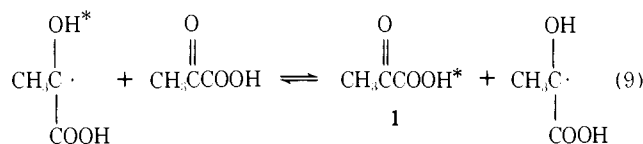
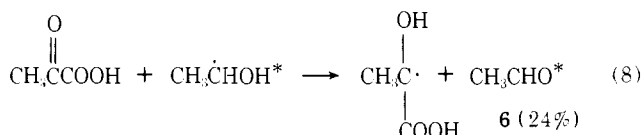
Formation of the second pair



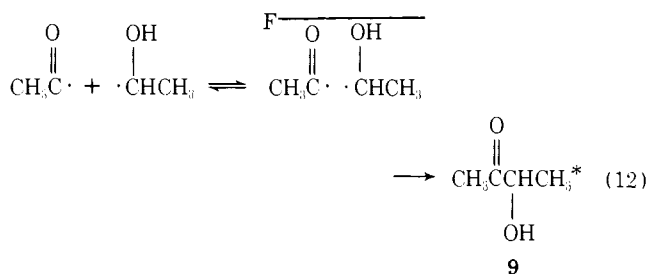
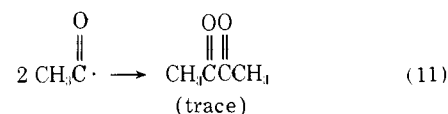
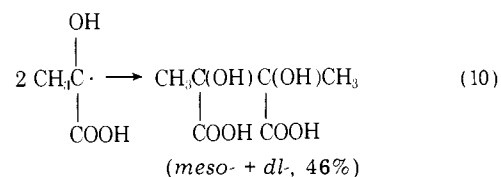
Geminate reactions of the second pair



Exchange reactions of radicals escaping from both pairs



Free radical termination reactions



The multitude of individual steps can be grouped into the general classifications shown. After formation of the initial radical pair (eq 3 and 4), four geminate combination and disproportionation processes (eq 5a-d) occur. Next, one of the products, acetaldehyde, gives rise to the formation of a second correlated pair (eq 6) and its subsequent geminate products (eq 7a-c). The escaping radicals from both pairs are converted efficiently to polarized diamagnetic products via exchange processes (eq 8 and 9), and the radicals are ultimately destroyed by uncorrelated pair dimerizations (eq 10-12).

The intricacy of the above scheme precludes an unambiguous evaluation of the relative contributions that particular elementary steps make to the observed polarizations of acetaldehyde and pyruvic acid. Both molecules are formed by four or more reactions generating diverse polarization phases. To confirm the singularity of the postulated mechanism it is necessary to dissect and appraise these separate components.

Table II. Isotropic Proton Hyperfine Coupling Constants and *g* Factors of Selected Free Radicals

Radical	Hyperfine coupling constant, ^a G				<i>g</i> factor	Ref
	α	β	OH	COOH		
CH ₃ Ċ(OH)COOH						
<i>cis</i> -		17.08	2.31	1.08	2.003 69	6b
<i>trans</i> -		16.47	2.00	0.84	2.003 74	6b
CH ₃ ĊHOH ^b	15.37	22.19	Unresolved		2.003 23	24
(CH ₃) ₂ ĊOH ^b		19.66	0.70		2.003 17	24
CH ₃ ĊO		5.1			2.0005	25
ĊOOH				0.9	2.0002	46

^a Consult text for assessment of signs. ^b Values measured at 26 °C.

Fortunately, the mechanism provides specific predictions which are amenable to experimental verification. Corroborating evidence is obtained first by establishing the multiplicity of the excited state precursor and the competing reactivity of the acetaldehyde generated during the reaction. Finally, it is possible to investigate independently the reactions of both correlated pairs.

The energy separations between the singlet (S₁) states and the triplet (T₀) states of pyruvic acid^{1b,2c} and naphthalene²⁶ ensure that triplet energy transfer from pyruvic acid to naphthalene will proceed at a rate approaching the diffusion-controlled limit,²⁷ while singlet quenching will be an extremely low probability process.²⁸ Under experimental conditions in which a minimum of 98% of the absorbed radiation excites pyruvic acid, very efficient quenching of the nuclear spin polarization is observed. This result clearly reaffirms the involvement of triplet state pyruvic acid in hydrogen abstraction from ethanol.^{5,6d,h}

The observation of strongly polarized 2-hydroxy-2-methylacetoacetic acid (**8**, eq 7a) during photolysis of equimolar solutions of pyruvic acid and ethanol is surprising. Fully cognizant of the selectivity of *tert*-butoxy radicals toward hydrogen abstraction from aldehydes over alcohols²⁹ and the analogies drawn between the abstraction reactivities of alkoxy radicals and n,π* triplet state ketones,³⁰ we did not anticipate that the low concentrations of acetaldehyde formed in the *initial* stages of reaction could compete so effectively for excited state pyruvic acid. The extent of this process is further demonstrated by the fact that **8** constitutes approximately 30% of the final product mixture. Evaluation of this reaction was complicated additionally by the observation that irradiation of pyruvic acid (0.10 M) in acetonitrile-*d*₃ also gives rise to polarized **8**, albeit much less efficiently (*vide infra*). Two independent modes of inquiry were pursued to clarify this matter.

The intensities of both the emissive and absorptive polarizations assigned to **8** were measured as a function of the initial ethanol concentration (0–0.5 M). The pyruvic acid concentration was fixed at 0.10 M. Both resonances attain a maximum intensity at approximately 0.15 M ethanol, decreasing smoothly at higher alcohol concentrations. These results are consistent with the postulated reaction of pyruvic acid with acetaldehyde. At the higher concentrations of alcohol the aldehyde would compete less successfully for the triplet state ketone, and the intensities of polarized **8** would be reduced.

The above reasoning is carried to its extreme by employing ethanol as the solvent. Continuous wave mode NMR experiments on solutions of pyruvic acid (0.20 M) in ethanol (20% C₆D₆ as lock) exhibit no polarizations corresponding to **8**. Suppression of this latter component of the mechanism permits direct observation of that component attributable solely to the reaction of pyruvic acid with ethanol. The polarizations observed for acetaldehyde are A + EA for the methyl protons and E + EA for the aldehydic proton—those phases predicted for the formation of acetaldehyde as an escape product (eq 8, Table I).

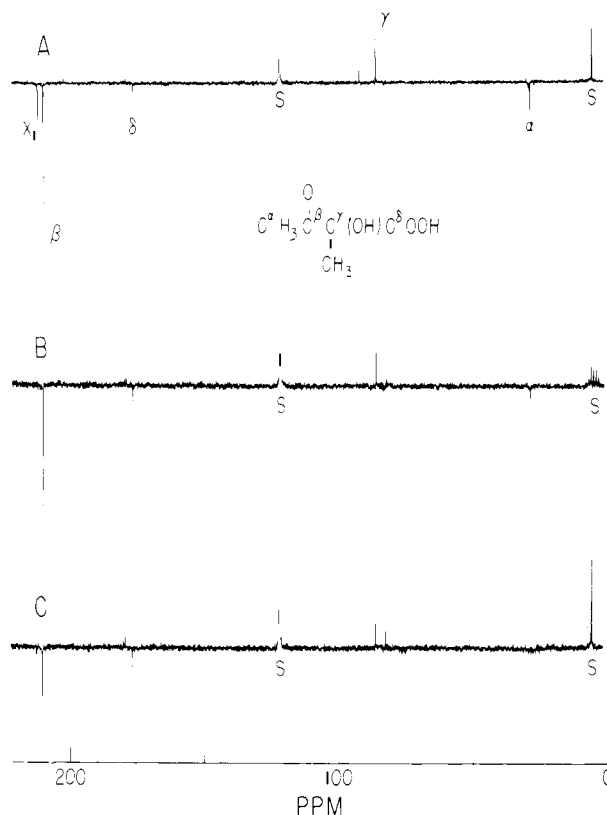


Figure 3. Proton noise decoupled 22.631-MHz ¹³C FT NMR spectra during irradiation of 0.50 M CH₃COCO₂H in the presence of selected additives: (A) CH₃CHO; (B) CH₃CH₂OH; (C) CD₃CD₂OD. S = solvent (CH₃CN and/or CD₃CN); consult footnote 31 for discussion of X₁.

Photolysis of pyruvic acid and ethanol-*d*₆ mixtures allows the acid methyl group to be traced through the reaction scheme unencumbered by other signals. Photooxidation of ethanol-*d*₆ must afford acetaldehyde-*d*₄ and its subsequent reaction with pyruvic acid requires incorporation of the CD₃CO moiety into **8**. Thus, the proton emission derived from **8** is predicted to vanish while the enhanced absorption should be unaffected. When the appropriate experiments were conducted the results clearly demonstrate that while the emission is strongly diminished in intensity, relative to the enhanced absorption, it does not vanish. Obviously there remains a residual contribution to the polarization from the acid condensation reaction previously noted.

Measurements of the proton-decoupled ¹³C nuclear spin polarizations within this system are instructive. Irradiation of pyruvic acid (0.50 M) in acetonitrile yields no discernible polarization. When ethanol (0.50 M) is added to the reaction mixture, strong polarizations attributable to **8** and consistent with eq 7a are observed (Figure 3). Both carbons of the acetyl group are predicted to be in strong emission: the hyperfine interactions to both atoms are large and of the same sign (+)

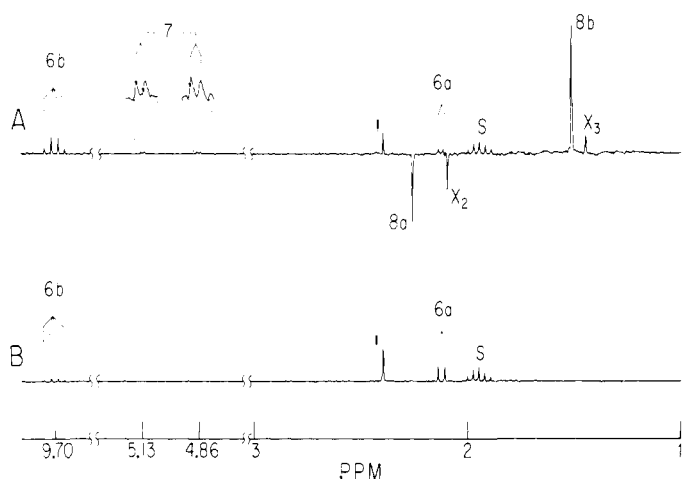


Figure 4. 90-MHz ^1H FT NMR spectra of 0.10 M CH_3COCOOH and CH_3CHO in CD_3CN : (A) during irradiation; (B) following irradiation. Assignments are summarized in Table I; consult footnote 31 for discussion of X_2 and X_3 ; S = solvent.

because of the σ character of the acetyl radical.²⁵ Within π radicals the spin densities upon carbon atoms adjacent to the radical center are small and only the carboxylate carbon is observed because of its long spin-lattice relaxation time. The spectral assignments are readily confirmed by comparison to the ^{13}C CIDNP spectrum (Figure 3) obtained upon photolysis of mixtures of pyruvic acid and acetaldehyde. Exploitation of ethanol- d_6 again yields explicit predictions. Introduction of the CD_3CO function now requires the high-field emission to become a septet and the carbonyl emission to be somewhat diminished in apparent intensity because of line broadening arising from long-range carbon-deuterium coupling. These expectations are fully borne out by experiment (Figure 3), and definitively establish that abstraction from acetaldehyde followed by geminate combination constitutes the predominant route to polarized **8**.

Clearly, the above mechanism may now be considered as some weighted combination resulting from two parallel primary processes. Dissection of the individual components is readily accomplished by model systems. The alcohol reaction may be verified by employing 2-propanol as the reductive substrate. The similarities of the rates of abstraction by triplet pyruvic acid from both alcohols^{6e,h} and of the magnetic parameters of the corresponding α -hydroxy radicals (Table II) ensure an unambiguous comparison. Furthermore, product acetone cannot suffer competitive abstraction.

Photolysis of mixtures of pyruvic acid (0.10 M) and 2-propanol (0.10 M) in acetonitrile- d_3 yields strong proton polarizations. The reactions involved are exactly analogous to those previously described for ethanol. All four geminate processes equivalent to eq 5a-d are observed with the predicted polarization phases (Table I). Most notably, pyruvic acid is unambiguously obtained in enhanced absorption as anticipated (eq 5d). Acetone is also found in enhanced absorption, reconfirming the conclusions of the CW mode experiments employing ethanol solvent as to the major path to oxidized alcohol (eq 8). Acetone (51%) and *meso*- and *dl*-dimethyltartaric acids (eq 10, 49%) are the sole detectable products.

The reaction of pyruvic acid with acetaldehyde is of course directly testable, and ^1H NMR spectra obtained during and following irradiation are illustrated in Figure 4. These results are in total accord with the prior mechanism (eq 6, 7, 9-11). The coupling product, **8**, is obtained in approximately 74% yield, thus allowing facile isolation and characterization of the methyl ester derivative. *meso*- and *dl*-dimethyltartaric acids comprise the remainder of the product mixture. Only trace

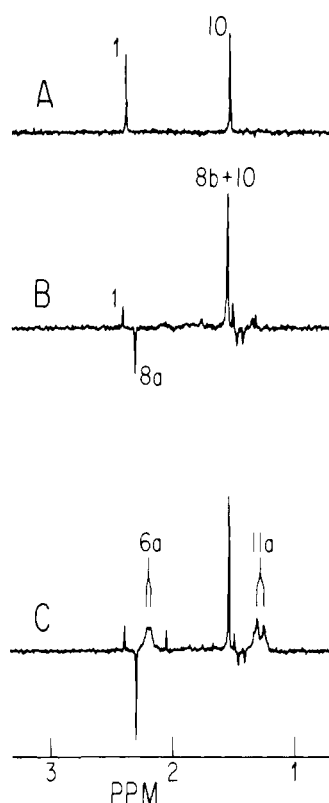


Figure 5. 90-MHz ^1H FT NMR spectra of 0.10 M CH_3COCOOH in D_2O : (A) following irradiation; (B) during irradiation; (C) during irradiation in the presence of CH_3CHO . Assignments are summarized in Table III.

quantities of biacetyl are detected by gas-liquid partition chromatography.

The totality of these results leads to the interesting conclusion that within the pyruvic acid-ethanol system the dominant polarization of both pyruvic acid and acetaldehyde arises from escape exchange reactions between the appropriate polarized radicals and ground-state pyruvic acid (eq 8 and 9).

Photoinitiated Decarboxylation of Pyruvic Acid. ^1H and ^{13}C NMR spectra obtained during and subsequent to photolysis ($\lambda > 310$ nm) of aqueous solutions (D_2O) of pyruvic acid are represented in Figures 5 and 6, respectively. Polarized spectra measured in the presence of added acetaldehyde are depicted for comparative purposes. Table III summarizes the spectral assignments and polarization phases.³¹

These spectra are obviously complicated by the equilibrium hydration of pyruvic acid and acetaldehyde.³⁶ This situation was aggravated within the product spectra, and interpretation was made even more difficult by expected incorporation of deuterium upon carbon. However, it is certain that no products corresponding to the polarized species are observed. Gas-liquid partition chromatography indicates acetoin to be the major organic reaction product in accord with prior investigations.^{2a,c} Minor amounts of biacetyl are detected, and formation of small quantities of *meso*- and *dl*-dimethyltartaric acids is presumed. The latter conclusion is consistent with ^1H and ^{13}C NMR analyses of the product mixtures. Evolution of carbon dioxide was readily monitored by chemical trapping with Ascarite. Analogous experiments conducted upon aqueous solutions of sodium pyruvate showed neither nuclear spin polarization nor detectable depletion of substrate.^{2c,3} The presence of conjugate base does not influence the photodecarboxylation of pyruvic acid.

Irradiation of pyruvic acid (0.10 M) in acetonitrile- d_3 or acetone- d_6 also yields proton polarization. The former system is illustrated in Figure 7 and results with acetaldehyde additive

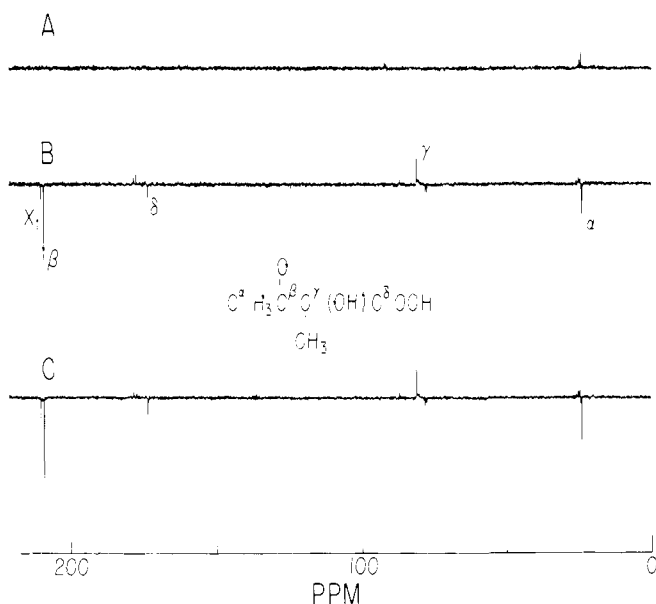


Figure 6. Proton noise decoupled 22.631-MHz ^{13}C FT NMR spectra of 1.0 M $\text{CH}_3\text{COCO}_2\text{H}$ in D_2O : (A) following irradiation; (B) during irradiation; (C) during irradiation in the presence of CH_3CHO . Consult footnote 31 regarding X_1 .

Table III. ^1H NMR Spectral Assignments and Polarization Phases: Pyruvic Acid in Deuterium Oxide or Acetonitrile- d_3

Spectral assignment ^a	Code no.	Polarization phase	
		Obsd	Predicted (eq)
$\text{CH}_3\text{COCO}_2\text{H}$	1	E	E (14)
$\text{CH}_3\text{C}(\text{OH})_2\text{CO}_2\text{H}$	10		
$\text{CH}_3\text{CH}^b\text{O}$	6a	E^b	E (7b, 7c)
	6b	A^b	A (7b, 7c)
$\text{CH}_3\text{CH}^b(\text{OH})_2$	11a		
	11b		
$\text{CH}_3\text{CO}^b\text{C}(\text{OH})\text{CH}_3^b$	8a	E	E (13)
CO_2H	8b	A	A (13)

^a Nuclear superscripts refer to code subclassifications. ^b Observed only in acetonitrile- d_3 containing acetaldehyde additive.

are again included for direct comparison (Table III). In both solvents conversion of pyruvic acid to products is quite inefficient, and quenching of the polarization upon addition of naphthalene indicates involvement of triplet state pyruvic acid. Experiments employing benzene- d_6 and dimethyl- d_6 sulfoxide solvents afford neither CIDNP nor discernible consumption of pyruvic acid. The latter instance presumably results from quenching of the excited state because no polarization is observed even in the presence of ethanol.

Scrutiny of Figures 5–7 indicates conclusively the identity of the polarizations observed with and without added acetaldehyde. The enhanced intensities of the polarizations in the presence of acetaldehyde confirm that the pyruvic acid–acetaldehyde reaction effectively contributes to the polarization.

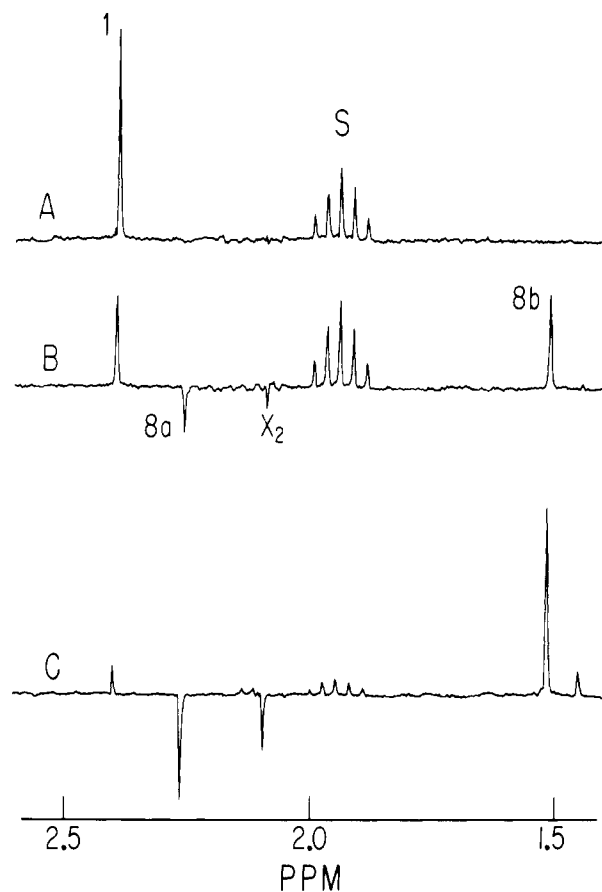
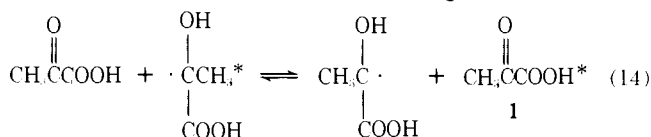
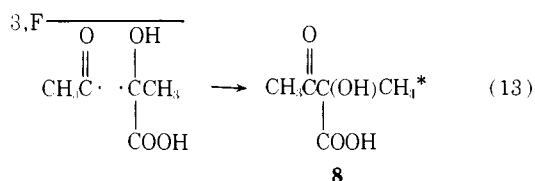


Figure 7. 90-MHz ^1H FT NMR spectra of 0.10 M $\text{CH}_3\text{COCO}_2\text{H}$ in CD_3CN : (A) following irradiation, vertical scale = 16K; (B) during irradiation, vertical scale = 16K; (C) during irradiation in the presence of CH_3CHO , vertical scale = 65K. Assignments are summarized in Table III; consult footnote 31 regarding X_2 ; S = solvent.

With prior knowledge of the results reported above, these experiments prove definitively that the nuclear spin polarizations observed upon photolysis of pyruvic acid in nonreducing environments arise from the radical pair composed of acetyl and pyruvic acid ketyl radicals. The genesis of that pair is less obvious: polarizations induced by the random encounters of uncorrelated radicals (F reactions) are qualitatively indistinguishable from those generated by triplet geminate pairs (vide infra).²³ Equations 13 and 14 reiterate the combination and escape exchange reactions affording polarized diamagnetic products. CIDNP phases required by the mechanism are in agreement with experiment (Table III). Attempts to prepare 2-hydroxy-2-methylacetoacetic acid (**8**) by an independent route and to measure its ^{13}C NMR spectrum in aqueous solution met with failure: the obtained spectrum was that of acetoin! Ethyl 2-hydroxy-2-methylacetoacetate provides an excellent spectral model for the parent acid in aqueous solution and supports the fortuitous degeneracy of the protons in enhanced absorption (**8b**) with the methyl group of hydrated pyruvic acid (**10**, Figure 5).

2-Hydroxy-2-methylacetoacetic acid has been the subject of various prior investigations,^{17,18} and it is well known that the molecule undergoes rapid acid-catalyzed hydrolysis to acetoin. The intermediacy of the obvious enediol has been postulated,^{18a} but the precise mechanism of this transformation is merely tangential to the present discussion. It only need be noted that in acetonitrile solution **8** is photochemically inert under the present experimental conditions. The conclusion is evident: acetoin is not a primary photoproduct of pyruvic acid in aqueous solution, but results from facile hydrolysis of **8**!

Table IV. Time Constants Defining Generation and Decay of Resonance Intensities from Polarized **8** in Acetonitrile- d_3 Solution

Experiment	Time constant, s ^a			
	Emission (8a)		Enhanced absorption (8b)	
	Generation	Decay	Generation	Decay
0.10 M CH ₃ COCOOH	6.96 ± 1.11 ^b	7.27 ± 0.49	2.94 ± 0.70	4.00 ± 0.16
0.10 M CH ₃ COCOOH + 0.10 M CH ₃ CH ₂ OH	17.78 ± 1.46	8.36 ± 0.39	6.73 ± 0.06	3.80 ± 0.94
Static T ₁		7.62 ± 0.56		2.32 ± 0.12

^a Average result of a minimum of three determinations. ^b Standard deviation.

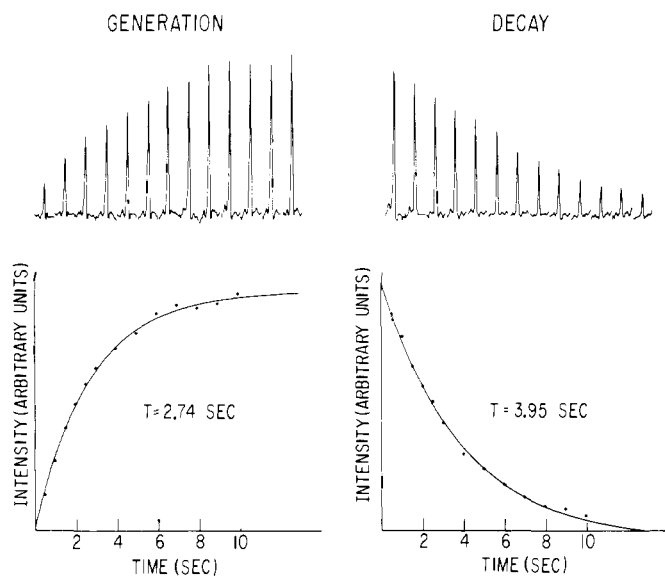


Figure 8. Time-dependent generation and decay of the proton enhanced absorption of polarized **8b** during light(t)- τ - $\pi/2$ irradiation of 0.10 M CH₃COCOOH in CD₃CN; (top) experimental signal intensities in arbitrary units, individual plot widths are 10 Hz; (bottom) computer fits of experimental intensities to the requisite theoretical exponential functions.⁸ Calculated time constants (T) are indicated.

action precludes corrections to eq 25 and 26 for product formation. Representative results for the enhanced absorption (**8b**) are illustrated in Figure 8 along with computer fits of the data to the appropriate theoretical exponential functions predicted by eq 25 and 26.⁸ Identical experiments were conducted upon samples of pyruvic acid (0.10 M) and ethanol (0.10 M) in acetonitrile- d_3 . Based upon steady-state intensities of polarized **8** and the extent of conversion of pyruvic acid to products, the rate of formation of acetaldehyde within this system must exceed that of Scheme III. Assessment of these time constants thus provide minimum deviations from the T_1 's that may be expected if Scheme III were operative. Decay constants must of course again follow T_1 . Finally, in situ preparation of **8** by photolysis of sealed samples of pyruvic acid and acetaldehyde in acetonitrile- d_3 allowed static measurements of the desired T_1 's by conventional inversion-recovery methods. Table IV summarizes the data. Despite the variations of some of the reported values,⁴⁴ the aggregate results are conclusive. Time constants describing the development of polarized **8** during photolysis of pyruvic acid are experimentally indistinguishable from the corresponding T_1 's as required by either Scheme I (eq 25) or Scheme II (eq 26). In contrast, generation time constants obtained in the presence of ethanol additive are significantly greater than $2T_1$. Scheme III is therefore excluded as a contributing primary process. While the large dynamic decay constants for **8b** are not readily rationalized,⁴⁵ they in no way compromise the present interpretation.

Inspection of eq 25 and 26 indicates that Schemes I and II may be differentiated by determining the kinetic order of the

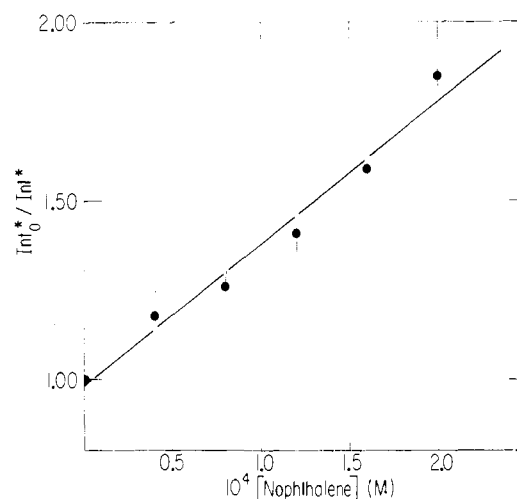


Figure 9. Relative effect of naphthalene concentration upon the intensity of the proton emission from polarized **8a** during irradiation of 0.10 M CH₃COCOOH in CD₃CN.

Table V. Slopes of the Stern-Volmer Quenching Plots for Various Concentrations of Pyruvic Acid

[CH ₃ COCOOH], M	Slope ^a × 10 ⁻⁴	
	Emission (8a)	Enhanced absorption (8b)
0.052	0.41 ± 0.03 ^b	0.39 ± 0.02 ^b
0.100	0.40 ± 0.02	0.42 ± 0.04
0.204	0.46 ± 0.01	0.45 ± 0.08

^a Calculated by computer fit of the averaged data from four experiments. ^b Standard deviation.

reaction with respect to pyruvic acid. The influence of varied pyruvic acid concentration upon the polarized signal intensities of **8** is most expeditiously examined by means of Stern-Volmer type quenching experiments. The advantage of such an approach is the fact that the analysis is not complicated by an explicit dependence upon the intensity of absorbed radiation. For a given substrate concentration, Scheme I (eq 25) predicts the following dependence upon quencher concentration, [Q]:

$$\frac{\text{Int}_0^*}{\text{Int}^*} = 1 + \frac{k_Q[\text{Q}]}{{}^3k_r + k_1[\text{CH}_3\text{COCOOH}]} \quad (27)$$

in which Int_0^* is the intensity in the absence of quencher and k_Q is the quenching rate coefficient. The slope of $\text{Int}_0^*/\text{Int}^*$ plotted as a function of [Q] would be $k_Q/({}^3k_r + k_1[\text{CH}_3\text{COCOOH}])$. Assuming 3k_r to be comparable to $k_1[\text{CH}_3\text{COCOOH}]$, Scheme I requires that the slope decrease with increasing pyruvic acid concentration. Scheme II (eq 26) obviously demands a zero-order dependence upon the substrate concentration, the slope being given by $k_Q/({}^3k_r + k_3)$.

The requisite experiments were conducted in acetonitrile- d_3 solution employing naphthalene as quencher. Figure 9 illustrates representative data for quenching of the emission from

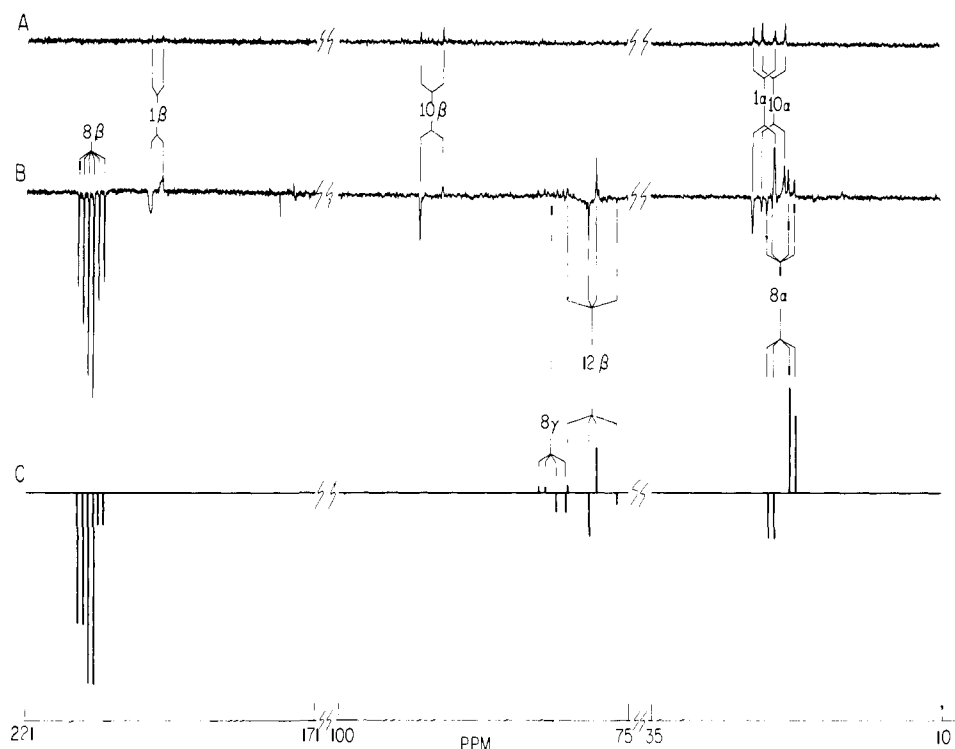


Figure 10. Proton noise decoupled 22.631-MHz ^{13}C FT NMR spectra of 0.10 M $\text{CH}_3\text{COCOOH-2,3-}^{13}\text{C}_2$ in D_2O : (A) following irradiation; (B) during irradiation; (C) simulated CIDNP spectra of $8\text{-}^{13}\text{C}_4$ and $12\text{-}^{13}\text{C}_4$,⁴⁹ intensities are normalized to the experimental spectrum assuming a line width of 3 Hz. Assignments are summarized in Table VI.

Table VI. ^{13}C NMR Spectral Assignments and Polarization Phases: Pyruvic Acid-2,3- $^{13}\text{C}_2$ in Deuterium Oxide

Spectral assignment ^a	Code no.	Polarization phase		
		Obsd	Predicted	
			Scheme II	Scheme I
$\text{H}_3\text{C}^{\alpha}\text{C}^{\beta}\text{OCOOH}$	1α 1β	EA E + EA	EA E + EA	E
$\text{H}_3\text{C}^{\alpha}\text{C}^{\beta}(\text{OH})_2\text{COOH}$	10α 10β	EA E + EA	<i>b</i> <i>b</i>	<i>b</i> <i>b</i>
$\text{H}_3\text{C}^{\alpha}\text{C}^{\beta}\text{OC}^{\gamma}(\text{OH})\text{C}^{\delta}\text{H}_3$ COOH	8	<i>b,c</i>	<i>b,c</i>	<i>b,c</i>
$\text{H}_3\text{C}^{\alpha}\text{C}^{\beta}(\text{OH})\text{C}^{\gamma}(\text{OH})\text{CH}_3$ COOH·COOH	12	<i>b,c</i>	<i>b,c</i>	<i>b,c</i>

^a Nuclear superscripts refer to code subclassifications, and a superior asterisk denotes ^{13}C . ^b Consult text. ^c Consult experimental and simulated spectra in Figure 10.

8α as a function of naphthalene concentration. Table V summarizes the measured slopes of the quenching plots as a function of pyruvic acid concentration. The identity, within experimental uncertainty, of the observed slopes provides direct evidence in support of Scheme II. Furthermore, if it is assumed that $k_3 \approx {}^3k_r$ and that energy transfer quenching is a diffusion-controlled process,²⁷ the rate coefficient for α -cleavage, k_3 , may be estimated to be on the order of $1 \times 10^6 \text{ s}^{-1}$ in acetonitrile solution.

A detailed analysis of Schemes I and II provides an additional, independent criterion by which the mechanistic possibilities might be distinguished. Scheme II contains a unique radical pair—the triplet geminate pair produced via the primary α -cleavage step (RP-3, eq 19). It is reasonable to anticipate that competitive with the designated escape processes,

RP-3 would be susceptible to geminate recombination (eq 20a) and/or disproportionation (eq 20b) thereby yielding polarized pyruvic acid and/or acetaldehyde. The essential feature is the virtual coincidence of the *g* factors of the radicals involved (Table II). That is, RP-3 can induce only multiplet effect polarizations.²³ With judicious manipulation of the experimental conditions Scheme I can rationalize formation of pyruvic acid exhibiting only net effect polarizations.

Pyruvic acid-2,3- $^{13}\text{C}_2$ was chosen for investigation, the additional spins serving to lift the degeneracies within the pyruvic acid spectrum as required for the observation of multiplet effects. The double label maximized the number of experimental degrees of freedom permitting study of spin systems ranging from AX to A_3X to A_3MX . The AX case was obtained by observing ^{13}C under conditions of ^1H noise decoupling. Discussion shall be limited to this single example as it is the most readily interpreted and is sufficiently defined to furnish all the required mechanistic information.

The predictions are straightforward. Equation 20a (Scheme II) demands EA multiplet phases for both the carbonyl and methyl carbons of pyruvic acid. The hyperfines on both carbons of the acetyl σ radical are large²⁵ and of the same sign (+), and J_{CC} is well known to be positive.⁴⁷ In contrast, Scheme I generates pyruvic acid only via reaction 14 involving the pyruvic acid ketyl radical which derives its polarization from RP-2. The methyl carbon of this π radical carries negligible hyperfine, and therefore the methyl carbon of pyruvic acid would not be polarized. Furthermore, because the carbonyl carbon is coupled *only* to a nuclear spin having no hyperfine, it can manifest only net polarization predicted to be emissive.⁴⁸ Reaction 14 is of course common to both mechanisms and a net emission superimposed upon the carbonyl EA multiplet is to be expected from Scheme II. The methyl carbon must retain its pure multiplet effect polarization.

Figure 10 illustrates the ^{13}C NMR spectra obtained during and subsequent to irradiation of aqueous (D_2O) solutions of pyruvic acid-2,3- $^{13}\text{C}_2$ (0.10 M), and Table VI summarizes the

spectral assignments. The multiplet effects observed for both the carbonyl and methyl carbons of pyruvic acid are immediately evident, and a net emission within the carbonyl multiplet is discernible. The correspondence with the predictions derived from Scheme II is exact! This additional evidence conclusively substantiates α -cleavage to be the primary photochemical process in decarboxylation of pyruvic acid.

Several remaining features of the spectrum represented in Figure 10B merit attention. The broadening of the pyruvic acid carbonyl carbon (8β) resonance is ascribed to a heating effect during sample irradiation. Independent variable temperature measurements are consistent with this rationale. The observation of CIDNP within the hydrated form of pyruvic acid (**10**) is not surprising. The polarization is merely carried over from pyruvic acid by the hydration process thus necessitating that the phases be identical with those of the respective nuclei of pyruvic acid (Table VI). The sole requirement is that hydration occur upon a time scale comparable to the spin-lattice relaxation times of the nuclei in question, that is, seconds.³⁶ The lack of polarized acetaldehyde (eq 20b) is noteworthy.

The qualitative phase rules²³ are ineffectual for analysis of the complicated ¹³C spin coupled systems of 2-hydroxy-2-methylacetoacetic acid (**8**, ABMX) and dimethyltartaric acid (**12**, AA'BB'). For this reason CIDNP spectra were calculated assuming that both products were derived from F-pair dimerizations of the requisite radicals (eq 13 and 10, respectively).⁴⁹ Direct comparison of the experimental and theoretical spectra (Figure 10) demonstrates that they are in reasonable agreement.

Conclusions

It is our opinion that elucidation of the mechanisms of photoreduction and photodecarboxylation of pyruvic acid demonstrates how powerful a tool CIDNP can be in mechanistic photochemistry. Many of the key reactions such as the hydrogen exchange reactions (eq 8 and 9) cannot be observed by conventional photochemical techniques. Similarly intermediates such as enol **7** and β -keto acid **8** will escape detection by product analysis because of their short lifetimes. However, it should also be pointed out that CIDNP, like any other mechanistic tool, has to be interpreted with caution. Concentration studies, general kinetic analyses, and product investigations are necessary before a reaction mechanism can be accepted. Given the complexity of the reaction sequences of the photoreduction of pyruvic acid, the interpretations of a previous study⁵⁰ of the same reaction under different conditions must be considered poorly supported. Thus, in our work on the photoreduction of pyruvic acid with the above-mentioned hydrogen donors and with lactic acid⁵¹ there is no evidence for the operation of a triplet mechanism⁵² for nuclear spin polarization. All observations are well explained with the radical pair mechanism, once the chemistry is understood.

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References and Notes

- (a) B. M. Monroe, *Adv. Photochem.*, **8**, 95-98 (1971); (b) J. F. Arnett, D. B. Larson, and S. P. McGlynn, *J. Am. Chem. Soc.*, **95**, 7599 (1973).
- (a) W. Dirscherl, *Hoppe-Seyler's Z. Physiol. Chem.*, **188**, 225 (1930); **219**, 177 (1933); (b) F. Lieben, L. Löwe, and B. Bäumer, *Biochem. Z.*, **271**, 209 (1934); (c) P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).
- P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **28**, 1160 (1963).
- G. F. Vesley and P. A. Leermakers, *J. Phys. Chem.*, **68**, 2364 (1964).
- D. S. Kendall and P. A. Leermakers, *J. Am. Chem. Soc.*, **88**, 2766 (1966).
- (a) T. Fujisawa, B. M. Monroe, and G. S. Hammond, *J. Am. Chem. Soc.*, **92**, 542 (1970); (b) A. Samuni, D. Behar, and R. W. Fessenden, *J. Phys. Chem.*, **77**, 777 (1973); (c) P. B. Ayscough and M. C. Brice, *J. Chem. Soc. B*, 491 (1971); (d) P. B. Ayscough, R. C. Sealy, and D. E. Woods, *J. Phys. Chem.*, **75**, 3454 (1971); (e) P. B. Ayscough and R. C. Sealy, *J. Photochem.*, **1**, 83 (1972); (f) *J. Chem. Soc., Perkin Trans. 2*, 543 (1973); (g) *ibid.*, 1620 (1973); (h) *ibid.*, 1402 (1974); (i) P. B. Ayscough, G. Lambert, and A. J. Elliot, *J. Chem. Soc., Faraday Trans. 1*, 1770 (1976).
- (a) G. L. Closs, *Adv. Magn. Reson.*, **7**, 157-229 (1974); (b) A. R. Lepley and G. L. Closs, Eds., "Chemically Induced Magnetic Polarization", Wiley-Interscience, New York, N.Y., 1973; (c) H. D. Roth, *Mol. Photochem.*, **5**, 91 (1973).
- Decay of polarization, $A_0 \exp(-t/T)$; generation of polarization, $A_\infty [1 - \exp(-t/T)]$; inversion-recovery, $A_\infty [1 - 2 \exp(-t/T)]$, where A_0 and A_∞ are the amplitudes at times zero and infinity, respectively; t is time (light(t) or τ); and T is the desired time constant.
- 37.9 mg $\text{CH}_3\text{COCOOH}/5$ mL D_2O ; path length 1.00 cm; $A = 0.574$. Apparent deviations from the Beer-Lambert law may be anticipated in D_2O because of the increasing extent of hydration with increasing total acid concentration. Total molar acid concentration, $K_d = [\text{CH}_3\text{COCOOH}]/[\text{CH}_3\text{C(OH)}_2\text{COOH}]$: 0.05, 0.74 ± 0.03 ; 0.10, 0.66 ± 0.03 ; 0.15, 0.62 ± 0.02 ; 0.30, 0.59 ± 0.01 ; 0.50, 0.58 ± 0.01 . Reported $(K_d)_{\text{D}_2\text{O}}$ values were measured by ¹H NMR at 28 °C. $(K_d)_{\text{H}_2\text{O}} = 0.41$ at 25 °C.³⁶
- "The Merck Index", 9th ed, Merck and Co., Rahway, N.J., 1976.
- O. Diels and E. Stephan, *Chem. Ber.*, **40**, 4336 (1907).
- 20% Carbowax 20M on 60/80 Firebrick, 10 ft \times 1/4 in., 60 mL/min.
- Preparative photolyses employed a medium-pressure mercury lamp (Hanovia 673A, 550-W) and Pyrex immersion chamber. All reactions were carried out under a nitrogen atmosphere.
- Contrary to prior reports,^{2c} the NMR spectra of both geometrical isomers are fortuitously coincident in aqueous solution (δ 1.52, TSP).
- T. J. deBoer and H. J. Backer, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 250.
- D. J. Robins and D. H. G. Crout, *J. Chem. Soc. C*, 1334 (1970).
- L. O. Krampitz, *Arch. Biochem.*, **17**, 81 (1948).
- (a) J. C. deMan, *Recl. Trav. Chim., Pays-Bas*, **78**, 480 (1959); (b) T. Nashina, *Nippon Kagaku Zasshi*, **80**, 900 (1959); (c) E. Juni, *J. Biol. Chem.*, **195**, 715 (1952).
- J. Carles, J. Layole, and A. Lattes, *C.R. Acad. Sci., Ser. D*, **262**, 2788 (1966); J. Layole, A. Lattes, G. C. Whiting, and J. Carles, *C.R. Acad. Sci., Ser. C*, **265**, 1277 (1967).
- N. Ogata, S. Nozakura, and S. Murahashi, *Bull. Chem. Soc. Jpn.*, **43**, 2987 (1970); J. W. Baker, *J. Chem. Soc.*, 520 (1942).
- L. N. Owen and H. M. B. Somade, *J. Chem. Soc.*, 1030 (1947).
- S. Schäublin, A. Höhener, and R. R. Ernst, *J. Magn. Reson.*, **13**, 196 (1974).
- R. Kaptein, *Chem. Commun.*, 732 (1971); ref 7a, pp 176-185.
- R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966).
- J. E. Bennet and B. Mile, *Trans. Faraday Soc.*, **67**, 1587 (1971).
- J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970, p 182.
- P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968); N. J. Turro and R. Engel, *Mol. Photochem.*, **1**, 235 (1969).
- S. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).
- C. Walling and M. J. Mintz, *J. Am. Chem. Soc.*, **89**, 1515 (1967).
- C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965); A. Padwa, *Tetrahedron Lett.*, 3465 (1964).
- A cursory examination of the spectra portrayed above indicates several ¹H and ¹³C NMR polarizations for which explicit assignments have not yet been offered. Those resonances labeled X₁ (¹³C, Figures 3 and 6), X₂ (¹H, Figures 4 and 7), and X₃ (¹H, Figure 4) will currently receive attention. The remainder continue to be elusive. Recollecting that X₁, X₂, and X₃ are obtained upon excitation of pyruvic acid with and without acetaldehyde additive, it is noteworthy that all three are also observed upon full arc irradiation of acetaldehyde in acetonitrile-d₃ solution. The acetyl radical is the only apparent species commonly shared by these diverse molecular systems, and it is therefore hypothesized that X₁, X₂, and X₃ are derived from secondary processes attributable to the acetyl radical. An obvious candidate is decarbonylation. While vapor-phase kinetic investigations⁵² imply that the cleavage of thermally equilibrated acetyl radicals would be insufficiently rapid at the bulk temperatures applicable to the present experiments, this exact process is observed in various matrices at 77 K.²⁵ Assuming decarbonylation, random phase diffusive encounters of acetyl and methyl radicals provide for the formation of polarized acetone. The magnetic parameters of the radicals involved (H_3C ; $g = 2.00252$, $a_{\text{H}} = 22.8$ G)³³ require emissive transitions from the protons of both methyl groups as well as the carbonyl carbon. X₁ and X₂ are both observed in emission, and standard proton spectra corroborate the assignment of X₂ to the methyl protons of acetone. Independent ¹H CIDNP investigations of the photochemistry of acetaldehyde and acetoin in benzene solutions are in full agreement with this deduction.³⁴ ¹³C reference spectra establish, however, that X₁ is found approximately 1 ppm downfield from acetone. A temperature effect altering the solvent lock frequency³⁵ during prolonged irradiation is rejected on direct experimental grounds. Thus, while X₁ and X₃ also logically appear to originate from the acetyl radical, no explicit assignments are forthcoming.
- J. G. Calvert and J. T. Gruver, *J. Am. Chem. Soc.*, **80**, 1313 (1958); J. G. Calvert, *J. Phys. Chem.*, **61**, 1206 (1957).
- R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
- B. Blank and H. Fischer, *Helv. Chim. Acta.*, **56**, 506 (1973).
- W. M. Litchman and D. R. McLaughlin, *Chem. Phys. Lett.*, **22**, 424 (1973).
- M. Becker and H. Strehlow, *Z. Elektrochem.*, **64**, 129 (1960); H. Strehlow, *ibid.*, **66**, 392 (1962); M. Eigen, K. Kustin, and H. Strehlow, *Z. Phys. Chem.*

- (Frankfurt am Main), 31, 140 (1962); R. P. Bell, *Adv. Phys. Org. Chem.*, **4**, 1 (1966).
- (37) L. J. Mittal, J. P. Mittal, and E. Hayon, *J. Phys. Chem.*, **77**, 1482 (1973).
- (38) The reduction of ground state pyruvic acid by $\cdot\text{COOH}$ is known to be an efficient process,³⁹ and a corresponding mechanism involving $\text{CO}_2^{\cdot-}$ has been postulated for photoinduced decarboxylation of the conjugate base of pyruvic acid in aqueous solution.⁴⁰
- (39) N. H. Anderson, A. J. Dobbs, D. J. Edge, R. O. C. Norman, and P. R. West, *J. Chem. Soc. B*, 1004 (1971).
- (40) (a) S. Steenken and D. Schulte-Frohlinde, *Angew. Chem., Int. Ed. Engl.*, **14**, 254 (1975); (b) S. Steenken, E. D. Sprague, and D. Schulte-Frohlinde, *Photochem. Photobiol.*, **22**, 19 (1975).
- (41) G. L. Closs and A. D. Trifunac, *J. Am. Chem. Soc.*, **92**, 7227 (1970).
- (42) R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5519 (1967); G. L. Closs and L. E. Closs, *ibid.*, **91**, 4549 (1969). A comprehensive discussion of the effects of relaxation upon CIDNP may be found in ref 7a, p 185 ff.
- (43) This statement is no longer valid for specific cases in which chain propagating steps yield nuclear spin polarization. Of course, it is strictly not possible to describe the relaxation of a coupled spin system containing more than two levels by a single relaxation time. The time constant in eq 25 and 26 should therefore be interpreted as an experimental decay constant instead of T_1 in the precise sense of its definition.
- (44) Time constants calculated for the light(t)- τ - $\pi/2$ experiments are inherently less accurate than those determined by inversion-recovery because of the diminished dynamic range of the requisite exponential functions.⁸
- (45) The possibility exists that the discrepancy between the T_1 measured by the inversion-recovery method and that obtained from the CIDNP method is indeed real. Theoretical justifications exist for different effective decay constants depending on the initial population patterns in a coupled multilevel system. The population distributions among the levels of the methyl protons are indeed different after a π pulse and after polarization in a CIDNP experiment. Work is in progress to examine this interesting problem.
- (46) R. O. C. Norman and P. R. West, *J. Chem. Soc. B*, 389 (1969).
- (47) (a) D. M. Grant, *J. Am. Chem. Soc.*, **89**, 2228 (1967); K. A. McLauchlan, *Chem. Commun.*, 105 (1965). (b) Decoupling experiments showed J_{CC} and J_{CH} to be of the same sign, and the latter is documented as being positive: A. D. Buckingham and K. A. McLauchlan, *Proc. Chem. Soc., London*, 144 (1963); R. A. Bernheim and B. J. Lavery, *J. Am. Chem. Soc.*, **89**, 1279 (1967); H. Spiessbeck, *Z. Naturforsch. A*, **23**, 467 (1968).
- (48) It might be suggested that disproportionation of RP-1 (Scheme I) could also yield polarized pyruvic acid. Arguments identical with those just presented imply that RP-1 would generate pyruvic acid exhibiting only net effects.
- (49) Spectra were calculated employing the following coupling constants: **8**, $J_{\alpha\beta} = +42$ Hz, $J_{\alpha\gamma} = -11$ Hz, $J_{\alpha\epsilon} = 0$ Hz, $J_{\beta\gamma} = +38$ Hz, $J_{\beta\epsilon} = -20$ Hz, $J_{\gamma\epsilon} = +34$ Hz, $a_\alpha = +49$ G, $a_\beta = +129$ G, $a_\gamma = +10$ G, $a_\epsilon = 0$ G; **12**, $J_{\alpha\beta}$ = +34 Hz, $J_{\alpha\gamma} = -6$ Hz, $J_{\alpha\epsilon} = 0$ Hz, $J_{\beta\gamma} = +40$ Hz, $a_\alpha = 0$ G, $a_\beta = +10$ G.
- (50) K. Y. Choo and J. K. S. Wan, *J. Am. Chem. Soc.*, **97**, 7127 (1975).
- (51) The observation of proton emission (i.e., diminished absorption) from the methyl singlet of pyruvic acid during photolysis of pyruvic acid-lactic acid mixtures in benzene solution⁵⁰ clearly constituted one of the major stimuli for rationalization of the photo-CIDNP of pyruvic acid by the so-called triplet mechanism.^{50,52} The argument was properly stated⁵⁰ that within high magnetic fields where S-T \pm mixing is negligible, no net effect polarization can be induced between identical radicals by the radical pair mechanism because of the vanishing Δg term.^{7a} By default the reported nuclear spin polarization was attributed to the triplet mechanism despite the fact that abstraction would have to occur on the nanosecond time scale in order to compete successfully with thermalization of the triplet sublevels. Lactic acid would, by necessity, also be found in net emission (possibly superimposed upon a pure AE multiplet effect from radical pair polarization), but no such result was reported. Investigations in this laboratory do not, however, support the previous experimental observations. Preliminary studies employing distilled syrup *d*-lactic acid in both benzene- d_6 and acetonitrile- d_3 solutions yielded pyruvic acid in enhanced absorption. Repeated purification by preparative GLC sharply decreased the polarization intensity indicating the intervention of an impurity reaction. L(+)-lactic acid was therefore chosen for further tests because of the greater ease with which this crystalline material could be rendered rigorously pure. Photolysis of pyruvic acid (0.10 M) in benzene- d_6 saturated with L(+)-lactic acid (0.028 M) afforded no nuclear spin polarization. No products could be detected following prolonged irradiation; thus there exists no evidence for the occurrence of reaction. Abstraction from lactic acid becomes an efficient process in acetonitrile with *meso*- and *d*-dimethyltartaric acids being readily formed. Photolysis of equimolar (0.10 M) mixtures of pyruvic and L(+)-lactic acids in acetonitrile- d_3 exhibited CIDNP attributable solely to the decarboxylation reaction of pyruvic acid previously described. Samples containing lactic acid were directly compared to pyruvic acid blanks. All signals from polarized and subsequent dark spectra were integrated, and normalized to the integral of residual CD_2HCN . The ratios of polarized **8a** and **8b** to polarized $\text{C}_2\text{H}_3\text{COCOOH}$ were identical under all circumstances. As well, the polarizations were totally insensitive to the presence of dissolved oxygen. The fact that decarboxylation competes with abstraction from lactic acid clearly indicates that the rate coefficient for the latter process cannot significantly exceed $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Under the experimental conditions of both the current and prior⁵⁰ investigations, generation of nuclear spin polarization via the triplet mechanism is neither observable nor theoretically tenable.
- (52) J. K. S. Wan and A. J. Elliott, *Acc. Chem. Res.*, **10**, 161 (1977), and references cited therein.

The Role of Substituents in Controlling the Mode of Intramolecular Cycloaddition of Nitrile Ylides¹

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Abstract: The intramolecular photocycloaddition reactions of a number of *o*-allyloxyphenyl substituted 2*H*-azirines have been examined in mechanistic detail. Upon irradiation with ultraviolet light, these systems undergo intramolecular 1,1- and/or 1,3-cycloaddition depending on the substituent groups attached to the 2 position of the azirine ring. The internal cycloaddition reactions have been shown to proceed through transient nitrile ylide intermediates. A kinetic investigation involving Stern-Volmer plots shows that the rate of internal 1,3-cycloaddition is three times faster than that of 1,1-cycloaddition. Inspection of molecular models of these *o*-allyloxyphenyl substituted nitrile ylides shows that two paths for cycloaddition are possible depending on the geometry of the nitrile ylide. The parallel plane approach of addends produces a 1,3 cycloadduct and occurs when the dipole possesses linear geometry. The alternate 1,1-cycloaddition process occurs when the dipole possesses bent geometry. Since the energy difference between the nonplanar bent and linear forms is very small, the preferred mode of cycloaddition will depend on the nature of the substituent groups attached to the nitrile ylide. According to recent MO calculations, methyl or other electron-releasing substituents on the 3 carbon of the ylide will increase the preference for the bent geometry and favor the 1,1-cycloaddition process. Placing electron-withdrawing groups at C-3 (i.e., CF_3 , H, $\text{C}_6\text{H}_4\text{NO}_2$) favors linearization of the nitrile ylide, thereby promoting 1,3-cycloaddition. The results show that when the energy difference between the nonplanar bent and linear forms is small, substituent effects can play an extremely important role in determining the course of the intramolecular cycloaddition reactions of nitrile ylides.

The monumental work of Huisgen and co-workers in the early 1960s led to the general concept of 1,3-dipolar cycloaddition.²⁻⁷ Few reactions rival this process in the number of bonds that undergo transformation during the reaction, producing products considerably more complex than the reactants.

Over the years this reaction has developed into a generally useful method of five-membered heterocyclic ring synthesis, since many 1,3-dipolar species are readily available and react with a wide variety of dipolarophiles.⁸ Perturbation theory⁹⁻¹⁶ has recently been shown to provide a powerful but simple