**Figure 1.** Predicted equilibrium geometries for the vinylidene and σ-bonded isomers of Al-C_2H_2. There are two conformers of the σ-bonded system, with the terminal hydrogen lying trans (the middle structure) or cis (the lowest structure) to the Al atom. Bond distances are in ångstroms.

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separated aluminum plus acetylene.[13] Configuration interaction including all valence electron single and double excitations (3461 configurations) reduces the dissociation energy of the vinylidene complex slightly, to 19.3 kcal. A correction for higher excitations (unlinked clusters)[14] provides our final ab initio prediction of 20.0 kcal for the Al-CCH$_2$ bond energy. The shorter (by 0.08 Å) Al-C internuclear separation for the vinylidene complex also attests to its stronger Al-C bond. Analogous CI studies of the trans-σ-bonded complex (6739 configurations) yield a binding energy of 7.5 kcal.

The vinylidene structure is inconsistent with Kasai, McLeod, and Watanabe's ESR spectrum; there may appear to be a conflict between theory and experiment. However, the barrier height between vinylidene and acetylene is ~8 kcal[8] and might not be greatly reduced by the presence of the Al atom. If this is the case, then the 1,2-hydrogen shift (eq 4) might not occur

$$\text{(structure)} \longrightarrow Al\text{—}C\text{≡}CH_2 \qquad (4)$$
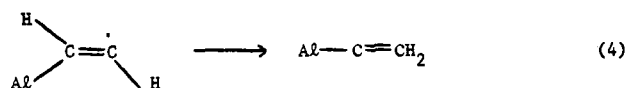
at all at the liquid helium temperatures of Kasai and McLeod.[2]

The most fascinating feature of the present study is that, while the isolated acetylene-vinylidene reaction is *endothermic* by 40 kcal, the same process becomes *exothermic* in the presence of an Al atom. We suspect that other endothermic reactions such as the methylcarbene-ethylene and methylnitrene-methylenimine rearrangements will also become favorable when complexation to a metal atom, metal cluster, or metal surface[6] is achieved. This general mechanism for using metal systems to transform endothermic reactions into nearly degenerate rearrangements may play a key role in catalysis and surface chemistry.

Laser Flash Photolysis with NMR Detection. Microsecond Time-Resolved CIDNP: Separation of Geminate and Random-Phase Processes

Sir:

The time resolution of conventional high resolution NMR spectroscopy is low because of the intrinsic properties of nuclear spin systems. Line-shape analysis for systems undergoing spin exchange overcomes this limitation to some extent.[1] Flow and stopped-flow methods permit direct kinetic measurements, but are at best restricted to reactions occurring over tens of milliseconds.[2] CIDNP provides information on chemical events taking place on a time scale ranging from 10^{-8} to 10^{-3} s by freezing this information into patterns of nuclear spin polarization within the diamagnetic reaction products.[3] This information is conveniently sampled on the time scale of the nuclear spin-lattice relaxation times of the products, that is, seconds. Kinetic analysis of data obtained under such steady-state conditions is, however, highly indirect and is dependent on many theoretical assumptions. We report here examples of time-resolved CIDNP with a resolution of 1×10^{-6} s, a time scale which allows the direct measurement of useful chemical kinetics. Ernst and co-workers have reported qualitatively similar experiments with a time resolution of 2.5×10^{-3} s.[4] These latter experiments were directed at specific dynamic nuclear spin phenomena[4a] and illustrate the observation of slow secondary reactions of diamagnetic transients.[4b]

The experiment, schematically represented in Figure 1, is in principle applicable to any system in which photolysis creates a radical pair. The sample is placed in the probe of a high resolution NMR spectrometer and is subjected to a series of radio frequency pulses randomly modulated in time and phase. This saturation pulse of ~50-ms duration totally destroys any nuclear magnetization thus eliminating all background signals.[5] The sample is then irradiated by an intense laser flash lasting several nanoseconds. The excited molecules generate radical pairs which induce nuclear magnetization by geminate and random-phase processes. The laser pulse is followed at any desired time interval, τ, by a radio frequency pulse creating a
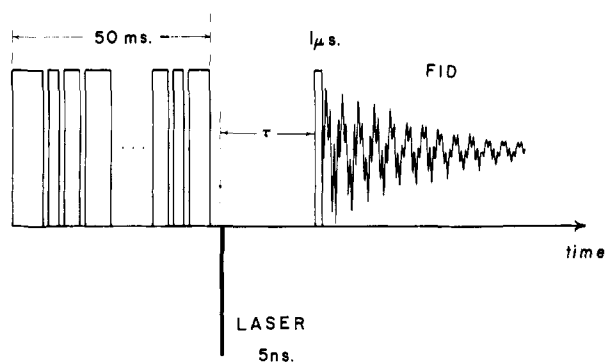
Figure 1. Schematic representation of the radio frequency and laser pulse sequence used in the time-resolved CIDNP experiment.
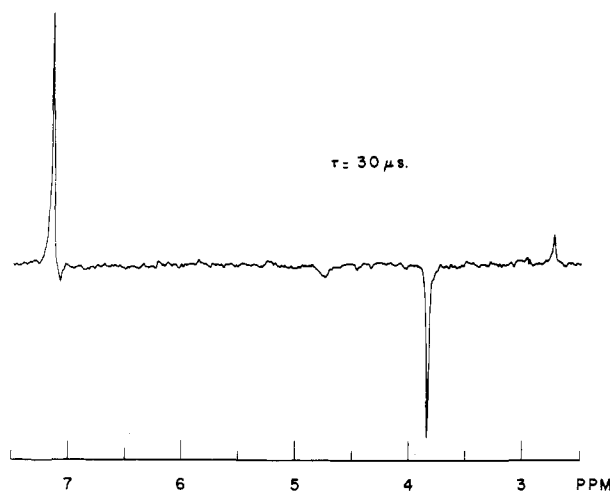

Figure 2. Typical 60-MHz spectrum obtained from the photolysis of a 2.8 × 10⁻³ M solution of ketone **1** in C₆D₆ containing 10% C₆H₆ after 2000 accumulations with a tip angle of 30° (1 μs). The signals at δ 2.7 and 3.8 ppm arise from the aliphatic protons of **2** and **1**, respectively. The absorption signal at 7.2 ppm is the C₆H₆ reference signal.[5]

Figure 3. Line intensities, normalized to C₆H₆ reference signal, of **2** (A) and **1** (B) as a function of delay τ. The signal intensities displayed in A have been expanded by a factor of 4. Conditions of photolysis are the same as given in the legend of Figure 2. The solid lines are arbitrary fits showing a half-time for the time-dependent part of the intensities of 24 ± 3 × 10⁻⁶ s. Results obtained for the signal of **1** in the presence of thiol scavenger are shown in C.

component of transverse magnetization. The resultant free induction decay (FID) of the polarized products formed at the application of the sampling radio frequency pulse is collected, and the entire sequence is repeated (∼10³ times) to achieve a sufficient signal to noise ratio. The time resolution of the present experiments is determined by the probing radio frequency pulse which is currently 1 × 10⁻⁶ s. Under these conditions only pure CIDNP intensities are observed, and their time evolution is governed by the various competing chemical processes destroying the freely diffusing radicals and by the loss of polarization by nuclear spin-lattice relaxation within the radicals.

The experiment is illustrated by the photolysis of benzyl phenyl ketone (eq 1 and 2),[6] with an NRG-0.7-5-200 nitrogen laser (5-ns fwhm). The radical pair produced by Norrish type
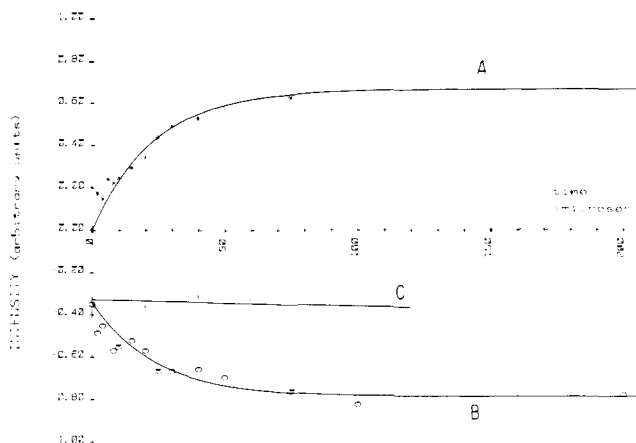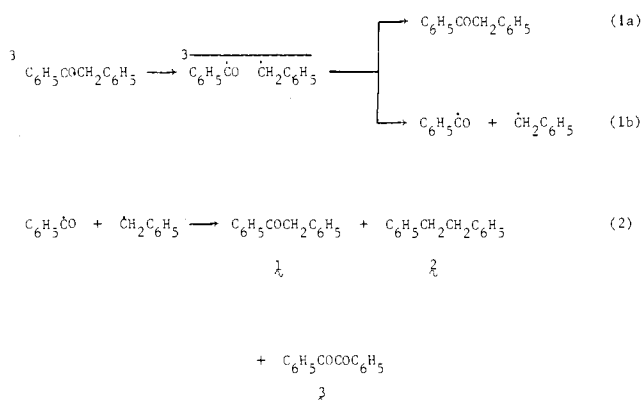
$$C_6H_5COCH_2C_6H_5 \xrightarrow{3} {}^{3}\overline{C_6H_5\dot{C}O \quad \dot{C}H_2C_6H_5} \begin{cases} \longrightarrow C_6H_5COCH_2C_6H_5 & (1a) \\ \\ \longrightarrow C_6H_5\dot{C}O + \dot{C}H_2C_6H_5 & (1b) \end{cases}$$

$$C_6H_5\dot{C}O + \dot{C}H_2C_6H_5 \longrightarrow \underset{\underset{1}{\sim}}{C_6H_5COCH_2C_6H_5} + \underset{\underset{2}{\sim}}{C_6H_5CH_2CH_2C_6H_5} \quad (2)$$

$$+ \underset{\underset{3}{\sim}}{C_6H_5COCOC_6H_5}$$

I cleavage consists of a benzyl radical and a benzoyl radical. The only geminate reaction regenerates the reactant (**1**, eq 1a), while diffusion and combination of uncorrelated pairs (F pairs) generates the starting ketone, bibenzyl (**2**), and benzil (**3**). The expected polarization patterns are emission (recombination polarization) for the methylene hydrogens of the ketone and enhanced absorption (escape polarization) for the aliphatic protons of bibenzyl. Figure 2 shows a typical spectrum obtained within 1-h accumulation time.

To understand the time evolution of the signals it is important to note that the ketone is produced by recombination of the geminate pairs as well as by combinations of F pairs, while bibenzyl can arise only via F pairs. It is therefore expected that the fraction of ketone generated via geminate pair collapse will be detected even at the shortest attainable delay (1 μs), while F pair generated bibenzyl and ketone will be detectable only at longer delays on a time scale of diffusion-controlled encounters. Figure 3 shows the buildup of ketone and bibenzyl signals as a function of time. This is the first direct observation of the predicted effect that F pairs enhance the polarization of geminate products if the reaction proceeds via triplet precursors.[7] In a control experiment dodecylthiol was added in concentrations sufficient to completely scavenge the free benzoyl radicals (5 × 10⁻³ M) preventing the formation of ketone via F pairs. As Figure 3 shows, under those conditions the ketone signal intensity is invariant with delay time.

Besides distinguishing random-phase from geminate processes, this technique should be capable of giving general kinetic information. For this it is desirable to reduce the time required for the sampling radio frequency pulse by at least one order of magnitude. Experiments toward that goal are in progress. The high resolution of NMR detection and the facility with which unique spectral assignments can be made should make this method a complimentary tool to more conventional optically detected flash photolysis.

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Book Reviews*

Aspects of Degradation and Stabilization of Polymers. Edited by H. H. G. JELLINEK (Clarkson College of Technology). Elsevier, Amsterdam. 1978. 690 pp. $124.50.

Fourteen contributed chapters deal with the properties of polymers relevant to their stability and with their modes of breakdown. Emphasis is on technical applications. Specific topics include mechanical degradation, effect of degradation on mechanical properties, reaction of polymers with pollutant gases, ignition of polymers and flame propagation, degradation processes in ablation, biodegradation, and degradation kinetics.

The Structure of Non-Crystalline Materials. Edited by P. H. GASKELL. Crane, Russak & Co., New York. 1977. 262 pp. $37.50.

A handsomely printed quanto-size volume containing the Proceedings of the Symposium held in Cambridge, England, 20–23 September, 1976, organized by the Society of Glass Technology. Fifty contributed articles provide a timely panoramic view of the structure and properties of amorphous systems, both experimental and theoretical aspects. A contribution by Nobel laureate N. F. Mott reviews electronic processes in glasses.

High-Power Lasers and Applications (Springer Series in Optical Sciences). Volume 9. Edited by K.-L. KOMPA and H. WALTHER. Springer-Verlag, Berlin. 1978. ix + 228 pp. $24.00.

Proceedings of the Fourth Colloquium on Electronic Transition Lasers at Munich, June 20–22, 1977. The main topics are high-power VUV, UV, and visible and IR lasers, with applications to nonlinear optics, chemical kinetics, isotope separation, and spectroscopy.

The Reward System in British and American Science. By JERRY GASTON (Southern Illinois University). Wiley/Interscience, New York. 1978. xiii + 204 pp. $18.95.

Do scientists receive recognition commensurate with their scientific contributions, free from the influence of extraneous social and political factors? The author's study of 600 British and American University physicists, chemists, and biologists indicates that they are indeed fairly rewarded for their productivity, instances to the contrary being statistically insignificant. The most accessible indicators of productivity—which should surprise none of the readers of this Journal—are number of publications and number of citations. A couple of interesting tidbits: Scientists have mean IQ's well above average but, beyond this threshold, there is practically no correlation between IQ and achievement. Also, the later productivity of scientists appears to be substantially influenced by the recognition accorded their early work as new Ph.D.'s.

Coordination Chemistry. Volume 2 (ACS Monograph, No. 174). Edited by A. E. MARTELL (Texas A & M University). American Chemical Society, Washington, D.C. 1978. x + 636 pp. $90.00.

Volume 2 treats the kinetics and mechanisms of reactions involving coordination compounds whereas Volume 1 (ACS Monograph No. 168, published in 1971) was more concerned with physical and chemical properties. The Monograph contains three chapters: 1. Kinetics and Mechanisms of Complex Formation and Ligand Exchange (Margerum, Cayley, Weatherburn, and Pagenkopf); 2. Ligand Reactions—The Effect of Metal Complexes on Chemical Processes (Hipp and Busch); 3. Oxidation–Reduction Reactions of Coordination Complexes (Pennington). Chapter 1 focuses on the reactions of the more labile metal ions and their complexes in aqueous solution. Chapter 2 views the known metal-affected reactions from a structural and mechanistic standpoint. Chapter 3, a full-scale review of oxidation–reduction chemistry, includes recent innovations in excited state and intramolecular electron transfer.

Atlas of Metal-Ligand Equilibria in Aqueous Solution. By J. KRAGTEN (University of Amsterdam). Wiley/Halsted, New York. 1978. 781 pp. $77.50.

A volume in the Ellis Horwood Series in Analytical Chemistry. This atlas gives computer-generated plots of side-reaction coefficients vs. pH for some 45 metals in the presence of 29 common ligands. The graphs for separate metal–ligand combinations are superposable to provide information on mixed ligands. Accompanying plots of pM' vs. pH show the regions of predominance of various species and indicate the conditions under which hydroxides will precipitate and polynuclear hydroxo complexes will form.

Ion-Selective Electrodes. Edited by E. PUNGOR and I. BUZAS. Elsevier, Amsterdam. 1978. iv + 613 pp. $75.00.

This volume contains the full text of papers presented at a conference held in Budapest, 5–9 September 1977. Seven plenary lectures covered recent trends in ion-selective electrode research, theoretical problems concerning the mechanism of electrode response, electrode construction and standardization techniques, and high-temperature applications. There follow some 48 discussion papers concentrating mainly on analytical applications of ion-selective electrodes. Topics discussed include transport characteristics and dynamical behavior of glass membrane electrodes, enzyme electrodes, liquid membrane electrodes, ion-exchanger electrodes, and incorporation of ion-selective electrodes into automated systems.

The Quest for Absolute Zero. 2nd Edition. By KURT MENDELSSOHN (Oxford). Wiley/Halsted Press, New York. 1977. 281 pp. $11.50 (paperback).

A charming account of the history of low-temperature research by an important contributor to the field. The book contains lucid semi-technical accounts of cryogenic techniques, thermodynamic and quantum principles near absolute zero, and the phenomena of superconductivity and superfluidity.

Chemistry and Physics of Carbon: A Series of Advances. Volume 13. Edited by P. L. WALKER, JR., and P. A. THROWER. Marcel Dekker, New York. 1977. viii + 295 pp. $32.50.

The volume consists of two chapters: The Optical Properties of Diamond (G. Davies) and Fracture in Polycrystalline Graphite (J. E. Brocklehurst). The effects of nitrogen impurities in diamond are considered in some detail. Author and subject indexes are appended.

Defects in the Alkaline Earth Oxides. By B. HENDERSON (Trinity College, Dublin) and J. E. WERTZ (University of Minnesota). Wiley/Halsted Press, New York. 1977. v + 159 pp. $20.00.

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* Unsigned book reviews are by the Book Review Editor.