attachment reaction was run. FTIR spectroscopy was used to confirm the presence of the ketone carbonyl stretch (1686 cm^{-1}) after the workup. Detection of the biradicals was accomplished by photolyzing a slurry of the modified silica in benzene (2 g of modified silica/100 mL of benzene) at 308 nm as the sample was pumped through a 1-mm quartz flat cell inside the cavity of a Varian E-9 X-band EPR spectrometer, which was equipped for direct detection as described previously[1b] except that the microwave bridge was modified to provide a faster time response.[5]

Direct detection EPR spectra of surface-bound biradical **2** produced by photolysis of ketone/silica system **1** are shown for several boxcar gate delay times in Figure 1A(i), and the simulated spectra, to be discussed below, are shown in Figure 1A(ii). These spectra are remarkably different from those from photolysis of a similar ketone in free solution, shown for comparison in Figure 1A(iii). For instance, the net absorption at early times is indicative of a strong triplet mechanism (TM) spin polarization, the first observation of this phenomenon in a mobile two-spin system.[6] The spectra also change shape much more drastically with time than do the solution spectra, and the line widths are clearly larger.

Simulation of the biradical spectra allows accurate determination of several important parameters: the initial populations of the triplet biradical spin states, the electronic spin–spin coupling J, and the encounter rate of the unpaired spins k_{en}. We make use of a well-established model for biradicals in solution.[7] The standard electronic basis set is employed: three triplet states (T^+, T^0, and T^-) which are nondegenerate in the applied field, and a singlet state (S) close in energy to at least one of the triplet levels and separated from T^0 by $|2J|$. Chemical reaction occurs only from the S state, which aquires a population from the triplet levels through nuclear hyperfine and spin–orbit coupling induced state mixing. The model is modified to account for the TM polarization passed on to the biradical from the parent ketone according to the model of Wong et al.[8] For the cycloalkanones used in this work, the TM will produce a net absorption.[9] Our simulation program stipulates that the initial triplet populations should sum to unity, and we let two of the three initial triplet populations become fitting parameters. Other adjustable parameters are the line width LW, the spin–spin coupling J, and the encounter rate k_{en}. The g factors and hyperfine coupling constants were taken from the literature values for the corresponding monoradicals.[10]

The simulations in Figure 1B are satisfactory with respect to both the overall shape and the time evolution of the EPR signal. The spectra are surprisingly sensitive to all five fitting parameters, and the very narrow range of error for LW, J, and k_{en} reported is an indication of the uniqueness of the fit. The value of k_{en} of $7.2 \times 10^{10}\ \text{s}^{-1}$ is almost *2 orders of magnitude larger* than the free-solution value of $1 \times 10^9\ \text{s}^{-1}$, and the J value is also larger than in solution (at this temperature in free solution, $J = -140 \pm 5$ MHz). Most likely the radical center closer to the surface has lost some of its rotational and translational degrees of freedom, removing access to conformations where the ends of the chain can best avoid each other. The line width is larger due to inefficient motional narrowing closer to the surface, a phenomenon also observed for monoradicals.[3]

An attempt to detect a spin-correlated radical pair whose members are anchored to two separate sites on the surface is shown in Figure 1B. Spin-polarized spectra are observed; however, they are extremely broad with no resolved hyperfine lines. The lack of features is indicative of multiple site occupancy, which stems from a lack of control of the attachment point in the synthesis of the precursor. The analogy in solution would be an EPR spectrum produced by a group of biradicals of many different chain lengths and therefore many different J couplings. However, it is interesting to note that the spin-polarization patterns evolves from predominantly absorptive to emissive/absorptive over just 300 ns, indicating that a fast k_{en} may also be present in this system.

The use of reactive biradicals as probes of diffusion phenomena in interfacial systems looks very promising with this powerful and informative experiment, and a detailed study of the effects of biradical chain length, solvent, temperature, surface morphology, and chemical composition is presently underway in our laboratories.

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Accurate Measurements of Proton Scalar Coupling Constants Using Carbon-13 Isotropic Mixing Spectroscopy[†]

S. Donald Emerson and Gaetano T. Montelione*

Center for Advanced Biotechnology and Medicine and
Department of Chemistry, Rutgers University
Piscataway, New Jersey 08854-5638

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Vicinal coupling constants provide information about molecular conformations in solution which is complementary to nuclear Overhauser effect data.[1] Particularly important are ${}^3J(\text{H}^\alpha\text{–H}^\beta)$ coupling constants which are used to determine stereospecific C^βH_2 assignments[2] and to characterize side-chain conformations.[2,3] In large peptides and small proteins, however, broad resonance line widths result in heavily overlapped cross-peak components and complicate measurements of the associated coupling constants.[4] One approach for overcoming this problem is two-dimensional (2D) homonuclear exclusive COSY (E.COSY).[5-7] These methods use linear combinations of multiple-quantum filtered COSY experiments,[5] mixing pulses with small (≪90°) flip angles,[6] or frequency-selective shaped pulses[7] to restrict magnetization transfer

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[*] Author to whom correspondence should be addressed.

[†] An initial description of this work was presented at the 32nd Experimental Nuclear Magnetic Resonance Spectroscopy Conference, April 10, 1991, in St. Louis, MO.

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to connected transitions. This results in simplified cross peaks with significantly less overlap between fine-structure components.

Homonuclear E.COSY experiments suffer from three significant shortcomings. First, the E.COSY cross-peak intensities are themselves conformation dependent and are often very weak or unobservable. Second, components within the H^{α}–H^{β} cross peaks are resolved in $\omega 1$ by the ca. 16 Hz $^2J(H^{\beta 2}$–$H^{\beta 3})$ splitting,[9] which is not much larger than typical proton line widths in small proteins (i.e., 5–20 Hz). Finally, these E.COSY experiments cannot be used to measure $^3J(H^{\alpha}$–$H^{\beta})$ coupling constants in amino acids which lack a geminal $H^{\beta 2}$–$H^{\beta 3}$ proton pair. Heteronuclear E. COSY experiments which use small angle ^1H pulses or frequency-selective soft pulses can also be used to determine the relative signs and magnitudes of homo- and heteronuclear coupling constants.[8] The C($\omega 1$)–C-selective–H($\omega 2$) experiment described here overcomes the inadequacies of these existing techniques by using a conformation-independent magnetization transfer pathway, separating the relevant cross-peak components by ca. 140 Hz in the $\omega 1$ dimension, and by exploiting heteronuclear spin topologies common to all amino acids with one or more H^{β} protons.

The pulse sequence for 2D C($\omega 1$)–C-selective–H($\omega 2$) spectroscopy is shown in Figure 1A. It uses ^{13}C isotropic mixing[10] followed by modified reverse-refocused INEPT.[11] For a uniformly ^{13}C enriched amino acid residue, the resulting spectrum exhibits cross peaks at $\omega 1 = {}^{13}C^{\alpha}$, $\omega 2 = H^{\beta}$ and at $\omega 1 = {}^{13}C^{\beta}$, $\omega 2 = H^{\alpha}$ with E.COSY-like fine structure (Figure 1B,C). These peaks are split in $\omega 1$ by $^1J(^{13}C^{\alpha}$–$H^{\alpha})$ (145 Hz) or $^1J(^{13}C^{\beta}$–$H^{\beta})$ (130 Hz), respectively, and in $\omega 2$ by the conformation-dependent $^3J(H^{\alpha}$–$H^{\beta})$ coupling of 7.8 ± 0.5 Hz. This same value of $^3J(H^{\alpha}$–$H^{\beta})$ was obtained from spectra processed with 1 Hz or 15 Hz of exponential line broadening in both dimensions, and is in excellent agreement with the ensemble-averaged value of 7 ± 1 Hz calculated from published Karplus curves[14] and the value of 7.2 ± 0.5 Hz measured in high-resolution 1D spectra.

The physical basis of the E.COSY-like pattern in these spectra is similar to that used recently for measuring $^3J(^{15}N$–$H^{\beta})$, $^3J(H^{\alpha}_{i}$–$^{15}N_{i+1})$, $^3J(H^{N}$–$H^{\alpha})$, and $^3J(H^{\alpha}$–$^{13}C^{\gamma})$ coupling constants.[15] For example, an $\omega 1 = {}^{13}C^{\alpha}$, $\omega 2 = H^{\beta}$ cross peak is created by the following sequence of events. First the $^{13}C^{\alpha}$ nuclei are frequency labeled during the evolution period, $t1$, in the presence of $^1J(^{13}C^{\alpha}$–$H^{\alpha})$ coupling. This results in two relevant populations of C^{α} magnetization; half of these C^{α} nuclei are coupled to H^{α} nuclei with spin angular momenta aligned with the applied magnetic field (referred to here as the ↑ spin ensemble) while the other half are coupled to H^{α} nuclei with spin angular momenta aligned against the applied magnetic field (the ↓ spin ensemble). Spin coupling to these two orientations of the H^{α} spin results in a splitting of the C^{α} resonance in the $\omega 1$ dimension of 145 Hz. Next, these two magnetization components are transferred to the C^{β} nucleus using a DIPSI-3 spin lock[12] and then to the attached H^{β} nuclei using a reverse-refocused INEPT sequence.[11] The distinction between ↑ and ↓ H^{α} spin ensembles is largely preserved by using a proton mixing pulse β with a small flip angle (i.e., 10°–30°) in the reverse-INEPT sequence (Figure 1A). The proton

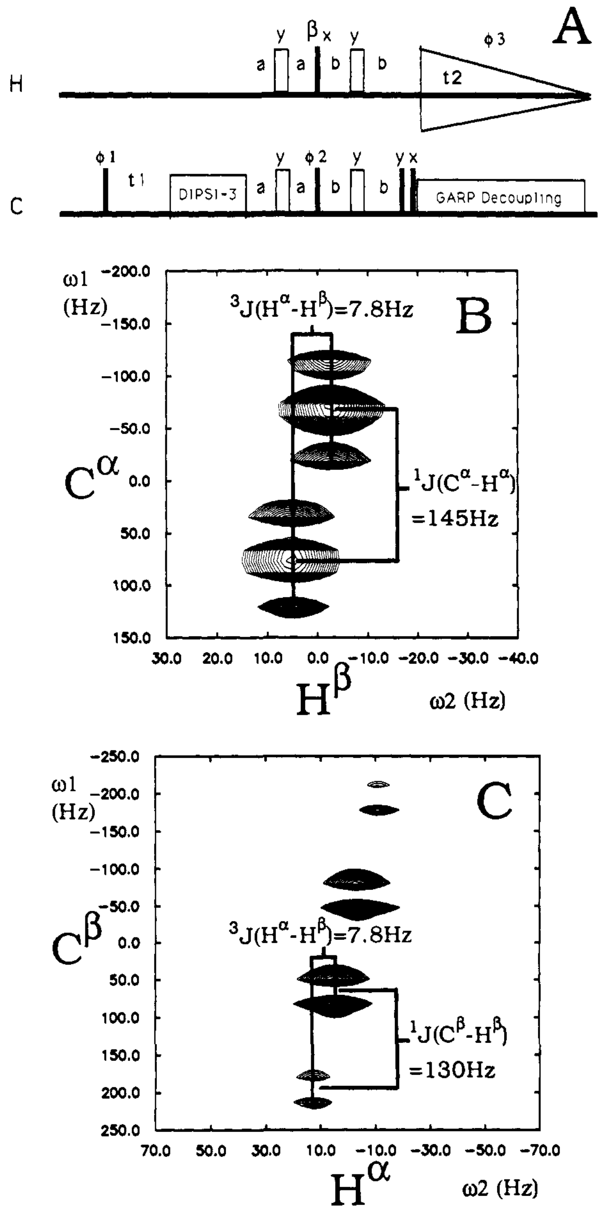

Figure 1. (A) Pulse sequence of the 2D C($\omega 1$)–C-selective–H($\omega 2$) experiment for measurements of homonuclear $^3J(H^{\alpha}$–$H^{\beta})$ coupling constants. The ^1H pulse width β is set to 10°–30°, and the delays are tuned in the following way: $a = 0.5$ ms, $b = 2.15$ ms. Spin locking for ^{13}C–^{13}C TOCSY is achieved using a 22-ms DIPSI-3 sequence.[12] The DIPSI-3 and GARP[13] multipulse sequences are executed by a waveform generator. The pulse phases are cycled as $\phi 1 = x, x, -x, -x$ and $\phi 2 = y, -y, y, -y$ and the receiver phase as $\phi 3 = +, -, -, +$. Time-proportional 90° increments of phase $\phi 1$ (TPPI) provides quadrature detection in $\omega 1$. (B) E.COSY-like cross peak at frequencies $\omega 1 = {}^{13}C^{\alpha}$, $\omega 2 = H^{\beta}$ from a 2D C($\omega 1$)–C-selective–H($\omega 2$) experiment on ^{13}C-enriched L-Ala. (C) E. COSY-like cross peak at frequencies $\omega 1 = {}^{13}C^{\beta}$, $\omega 2 = H^{\alpha}$ from the same spectrum. These spectra were obtained on a sample of 100% uniformly ^{13}C enriched L-Ala (MSD Isotopes) in ^2H_2O using a proton pulse β = 30°. The data were collected on a Varian Unity 500 spectrometer using 700 TPPI increments of eight scans each and were processed with 15 Hz of line broadening in both dimensions in order to simulate the effects of broad line widths on the estimated values of $^3J(H^{\alpha}$–$H^{\beta})$. The same value of $^3J(H^{\alpha}$–$H^{\beta})$ was obtained using a proton pulse β = 10°.

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magnetization is then detected in $t2$ while using broadband ^{13}C decoupling with GARP.[13] During the detection period, the $\uparrow$ and $\downarrow$ ensembles of the H^{β} spins (corresponding again to the two spin states of H^{α}) precess with a frequency difference of $^{3}J(H^{\alpha}-H^{\beta})$. The E.COSY-like pattern results from a correlation of the $\uparrow$ and $\downarrow$ ensembles of the C^{α} during $t1$ with the corresponding $\uparrow$ and $\downarrow$ ensembles of H^{β} during $t2$. A similar process acting on the magnetization which begins on C^{β} gives rise to E.COSY-like structure in the $\omega 1 = C^{\beta}$, $\omega 2 = H^{\alpha}$ cross peak.

In conclusion, 2D $C(\omega 1)$–C-selective–$H(\omega 2)$ spectroscopy is a simple approach for determining ^{1}H homonuclear coupling constants in ^{13}C-enriched molecules. In principle, the experiment can also be used to measure homonuclear coupling constants of ^{13}C-enriched ligands bound to proteins. It represents one of an expanding group of multidimensional NMR methods[15] for obtaining extensive sets of homo- and heteronuclear vicinal coupling constants in polypeptides and proteins.

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Note Added in Proof. Since submitting this paper for publication, we have found that this pulse sequence can be used for determining $^{3}J(H^{\alpha}-H^{\beta})$ coupling constants in a small ^{13}C-enriched protein and in long amino acid side chains. We have also developed modified 2D and 3D versions which utilize initial polarization transfer from ^{1}H to ^{13}C to enhance the sensitivity of the experiment (Emerson and Montelione, manuscript in preparation).

Registry No. Ala, 56-41-7; Thr, 72-19-5; Val, 72-18-4; Ile, 73-32-5.

Hydrogen Isotope Effect and Traveling Waves in a Halogen-Free Chemical Oscillatory System

Paul Rys* and Junkuan Wang[1]

Laboratorium für Technische Chemie
Eidgenössische Technische Hochschule (ETH)
ETH-Zentrum, CH-8092 Zurich, Switzerland

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Chemical oscillators and periodic spatial propagation of reaction fronts have received increasing attention.[2-15] A detailed examination of complex chemical reaction systems in their oscillating mode may indeed lead to valuable new mechanistic insights into the nature of the selectivity-determining interplay of diffusional and chemical events.

In 1983, Jensen reported oscillations during the Co(II)-catalyzed air oxidation of benzaldehyde in aqueous acetic acid in the presence of bromide ion.[16] Since then, many attempts have been made to describe the complex chemistry of this system.[17-22] Thus far, three different mechanistic models have been proposed[17,19,21] and used to simulate the oscillatory behavior of the Jensen system by computation.[19,20,22]

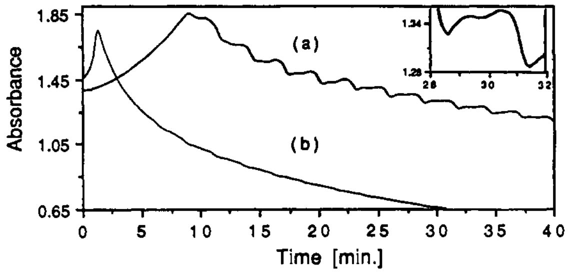

Figure 1. Oscillations in absorbance of Co(III) at 620 nm in a closed system at 60 °C, initially containing [Co(III)] = 8.0 × 10^{-3} M, [Co(II)] = 2.5 × 10^{-3} M, and [PhCRO] = 0.15 M. The total volume of the reaction mixture in the cell is 3.2 mL: (a) PhCDO; (b) PhCHO; inset, enlargement of the segment of absorbance curve a between 28 and 32 min.

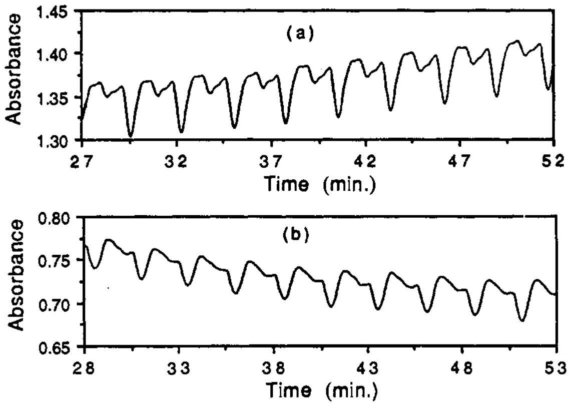

Figure 2. Oscillations in absorbance of Co(III) at 620 nm in an open system at 60 °C, initially containing [Co(III)] = 8.0 × 10^{-3} M, [Co(II)] = 2.5 × 10^{-3} M, and [PhCRO] = 0.15 M: (a) PhCDO; (b) PhCHO.

The recent studies[22,23] prompt us to report here the discovery of an oscillatory system which exhibits the following periodic and mechanistic features: (i) The system is based on the autoxidation of benzaldehyde; however, unlike the Jensen oscillator, it is entirely halogen-free. (ii) Our chemical oscillator reveals a considerable kinetic hydrogen isotope effect, which is particularly fascinating. We are able to demonstrate for the first time that an oscillatory behavior can be modulated by taking advantage of an isotope effect. (iii) The present oscillatory system exhibits its chemical periodicity not only in time but also in space: self-generated chemical waves propagating through the motionless reaction mixture have been observed. Although it has already been demonstrated[22,23] that a single propagating reaction front of Co(III) could be initiated in a similar system, we do not recall having yet seen any experimental report on periodically self-generating reaction waves in the autoxidation of benzaldehyde.

The fact that all of these features are displayed in the same system makes the present oscillator particularly attractive for

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