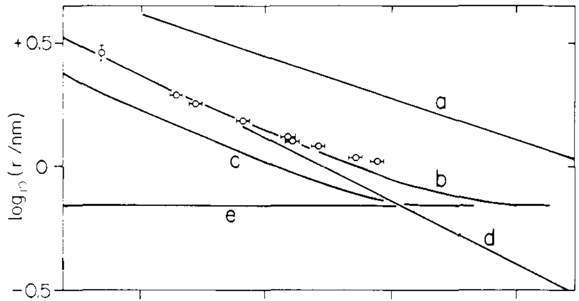

Figure 1. Plot of EPR double integral vs. mean nearest-neighbor distance $\bar{r}$ (obtained from dipolar broadening) for **3** under methanol at 77 K. The theoretical curves a–e are discussed in the text. The error bars indicate the precision of measurement of d_1/d and the double integrals.

of ρ_{NH_2}, it was found that, when ρ_{NH_2} was low, monoalkylation was complete. However, when ρ_{NH_2} was high, monoalkylation was incomplete based on **1**; the maximum ρ_{SL} obtained, 1.5 nm^{-2}, was consistent with a single molecular layer of nitroxide moieties close packed in two dimensions.

There are a number of possible methods for determining spin-spin distances. If the orientations of the spin-spin vectors are random with respect to the magnetic field and the rates of molecular reorientation and electron and ^{14}N spin-lattice relaxation are slow, the contribution to the line width from dipolar coupling is a function of the microscopic spin-spin distances. If the spins are dilute, this dipolar broadening arises almost entirely from nearest-neighbor couplings. On the other hand, trivially, the EPR double integral is a macroscopic quantity dependent only upon the average ligand density and independent of the spatial distribution. Thus, a comparison of nearest-neighbor distances (obtained from dipolar broadening) with the EPR double integral should indicate whether the ligand distribution deviates from randomness.[8]

The spectral parameter[9] d_1/d was used as a measure of dipolar broadening. It is a linear function both of the intrinsic line width (i.e., that part not due to A and g anisotropy) and of the concentration of homogeneous frozen methanol solutions of **2** below 250 mmol L^{-1}. From the latter dependence, the relationship between d_1/d and $\bar{r}$, the mean nearest-neighbor distance, was found.

In Figure 1 is shown a plot[10] for **3** under methanol of $\bar{r}$ (obtained from d_1/d at 77 K) against the EPR double integral. The theoretical curves represent (a) spins randomly distributed in three dimensions throughout the entire pore volume (0.65 mL g^{-1}) of the sample; (b) spins, associated with an effective molecular area[11] of 0.5 nm^2, randomly distributed over the entire measured surface area (2.17 × 10^{20} nm^2 g^{-1}); (c) same as (b), but only half the surface was available for spin labeling; (d) same as (b), but nitroxides have zero molecular area; (e) spins, having an effective molecular area of 0.5 nm^2, distributed in patches of closely packed ligand. Clearly hypothesis b, random two-dimensional distribution with correlation by molecular volume, agrees well with the data. The deviation from (b) at high ρ_{SL} probably arises from our neglect of non-nearest-neighbor dipolar couplings (there are proportionally more of these in three than in two dimensions). Since this deviation is in the direction of high $\bar{r}$, it is unlikely to reflect a deviation from randomness. Hypothesis e, which corresponds, for example, to a model in which the 3-aminopropyl ligands do not bind covalently to the surface but exist in patches of tightly adsorbed oligosiloxane so that d_1/d is insensitive to ρ_{SL} is clearly excluded.

The high sensitivity of EPR spectroscopy, combined with the ready availability of methods for spin labeling a wide variety of organic functionality, promises to ensure that this technique has widespread applicability. Studies on other surfaces including cellulose and biological membranes are in progress in this laboratory.

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Sequential Oscillations in Mixed-Substrate Belousov–Zhabotinskii Systems

Sir:

The Belousov-Zhabotinskii (BZ) reaction[1] is the most thoroughly characterized of the known nonbiological oscillating chemical reactions.[2] A large number of organic substrates[3,4] have been found to give rise to oscillations when combined with appropriate metal catalysts and concentrations of bromate and sulfuric acid in the BZ reaction. Different substrates produce a considerable variation in such features

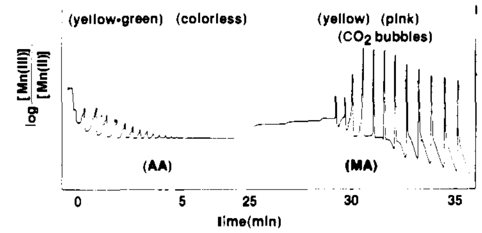

Figure 1. Oscillations in a mixed MA–AA system. Initial concentrations: [H_2SO_4], 0.93 M; [$KBrO_3$], 0.07 M; [$MnSO_4$], 0.017 M, [AA], 0.015 M; [MA], 0.035 M. Note the shoulders and color changes described in the text.

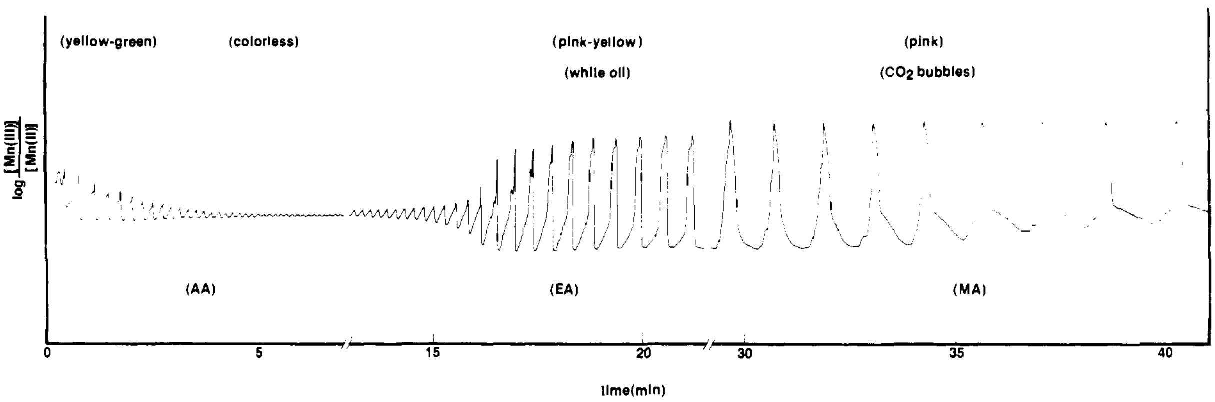

Figure 2. Oscillations in the three-substrate MA–AA–EA system. Initial concentrations: inorganic species as in Figure 1; [AA], 0.0125 M; [MA], 0.0125 M; [EA], 0.025 M.

as the wave form, frequency, amplitude, and duration of oscillations.

It is of some interest to consider how the BZ reaction might behave if more than one organic substrate were present. Possible modes of behavior include (a) inhibition of oscillation; (b) independent, concurrent oscillation, perceived, for example, as beats, modified wave forms or chaotic fluctuations; (c) entrainment, i.e., oscillations generated by a single substrate which "drive" the other substrate reactions to follow the dominant rhythm, resulting possibly in enhanced amplitude of oscillation; (d) sequential oscillation, in which the system first uses one substrate almost completely and then, perhaps after a transition period, consumes the next substrate. The existing simple models of the BZ system, such as the Oregonator,[5] contain too little detail to allow an unambiguous prediction of which type of behavior to expect, while inclusion of multiple substrates in a fuller model[6] would require considerably more knowledge of the chemistry of the organic intermediates than is now available.

In this communication, we present experimental evidence that, in at least some mixed-substrate BZ systems, sequential oscillations are the dominant form of behavior. We have employed manganous sulfate as the catalyst and use three different substrates: malonic acid (MA, $CH_2(COOH)_2$), acetylacetone[3a] (AA, $CH_3COCH_2COCH_3$), and ethyl acetoacetate (EA, $CH_3COCH_2COOC_2H_5$). Oscillations were monitored by following the redox potential of the solution between a platinum electrode and a double junction reference electrode as well as the bromide concentration with a specific ion electrode. All reactions were carried out at 31 °C.

Each substrate when used alone in the BZ reaction gives rise to characteristic features which enable us to identify its oscillation in the mixed systems. MA oscillations are characterized by nearly constant amplitude, a shoulder on the right side of the peaks, alternation of pink and colorless solution, and the production of CO_2 bubbles. The AA oscillations show decreasing amplitude, a shoulder on the left of the peaks, yellow-green to colorless solutions, and, at certain concentrations, a "null period" during which the potential and $[Br^-]$ are nearly constant for ~20 min to 2 h before concentration fluctuations resume. This last phenomenon will be discussed in more detail elsewhere. EA oscillations (which have not been previously reported in the literature) have a nearly symmetric wave form, resemble MA oscillations in color and constancy of amplitude, and are accompanied by the production of a white oil, which is shown by NMR to be the dibrominated product $CH_3COCBr_2COOC_2H_5$. Induction periods for all three substrates are quite short (<2.5 min) and obey the relation

$$t_{AA} < t_{EA} < t_{MA} \qquad (1)$$

over a wide range of concentrations. Amplitudes of oscillation follow the same order as in eq 1.

In Figure 1, we show the behavior of a mixed AA–MA system. The wave form, amplitude, and color clearly show the initial oscillations to be of the AA type, while the same considerations, plus the appearance of CO_2 bubbles, characterize the second set of oscillations (after a brief mixed or transition state) as MA generated. The null period, which appears in AA–MA and AA–EA, but not in EA–MA mixtures, is also evident. Similar sequential oscillations were also observed in AA–EA and EA–MA systems. When the concentrations of the two substrates are varied, the duration, frequency, and amplitude of the two sets of oscillations as well as the length of the transition period and the null period (if AA is present) change. However, at all concentrations and substrate combinations for which one can identify a sequential progression, AA oscillations occur first and MA oscillations last. As a more dramatic example, we show in Figure 2 the three-substrate system. Again, the sequential nature of the oscillations and the ordering according to eq 1 are preserved.

Sequential oscillations have also been observed[7] in mixed BZ systems using a cerium catalyst and other substrates. The glyoxylic acid–MA system studied by Kaner and Epstein[8] would appear to show entrainment (type c) behavior, though the glyoxylic acid oscillations may not be of the BZ class[8] and/or the bromate level may fall too low under the conditions employed to support further oscillations after the glyoxylic acid oscillations have ceased. Whether sequential oscillation is the general case in mixed-substrate systems (e.g., in glycolytic oscillation[9]) and whether a single kinetic property, such as the length of the induction period (eq 1) or a single thermodynamic parameter, such as the redox potential, as in an electrolytic separation, is always an accurate predictor of the order in which the different oscillations occur, are questions that will require further experimental and theoretical investigation.

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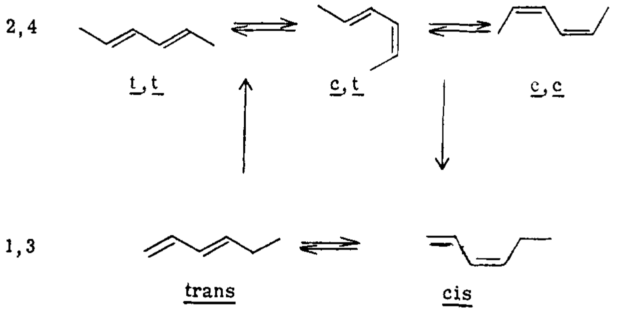
Laser-Induced Infrared Multiphoton Isomerization of Hexadienes

Sir:

It has recently been demonstrated that polyatomic molecules can undergo chemical change as the result of multiphoton absorption phenomena occurring in an intense infrared laser field.[1] Isotopic enrichment of a number of chemically and technologically important isotopes has been achieved by this technique.[2] Isotope enrichment requires the selective excitation and reaction of one component of an isotopic mixture. Frequency selective excitation of polyatomics is achievable owing to the finite vibrational normal mode frequency shifts of different isotopic compounds. Excitation is normally carried out at low pressures to avoid collision induced energy randomization among absorbing and nonabsorbing isotopic molecules. Selective excitation and reaction of structural and configurational isomers of polyatomic molecules with finite vibrational normal mode frequency shifts are also feasible.[3] Since the energy barriers for isomerization processes are frequently well below bond dissociation energies, it should be possible to effect clean, nondestructive isomerization of absorbing isomers to nonabsorbing isomers. The vibrational energy level density in the energy region required for facile isomerization is significantly lower than that in the region near the dissociation energy.[4] This intermediate excitation region is one for which very few probe techniques currently exist and is a region in which energy-transfer phenomena are not well understood. Thus isomer selective multiphoton infrared excitation offers potential both as a synthetic technique and as a probe of molecular dynamics.[5]

We report here the preliminary results of our investigation of the isomer specific infrared laser excitation and reaction of the three conformational isomers of 2,4-hexadiene (trans,trans, cis,trans, and cis,cis) and their structural isomers, the 1,3-hexadienes (trans and cis) (Scheme I). Among the significant findings of this investigation are (a) selective and nondestructive conversion of absorbing to nonabsorbing isomers, (b) preparation of isomer mixtures significantly enriched in the thermodynamically less stable isomers, and (c) the measurement of single-pulse product ratios which appear to be indicative of two or more successive isomerization processes occurring within or shortly after a single laser pulse.

Scheme I



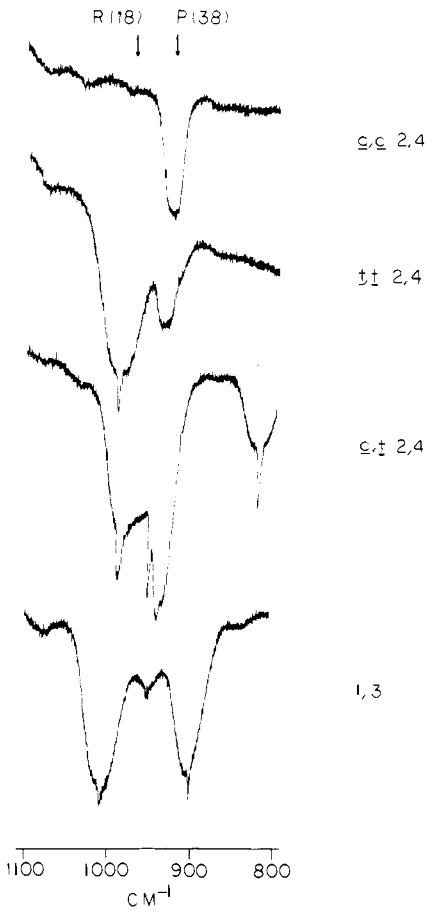


Figure 1. Infrared spectra of the hexadiene isomers in the 800–1100-cm^{-1} region. Spectra were taken at 20-Torr pressure in a 10-cm cell. Peak absorption of *cis,cis*-2,4-hexadiene is ~40%; other isomers are on the same scale.

The isomeric hexadienes were obtained from Chemical Samples Corp. and used without further purification. The isomeric 2,4-hexadienes were of >98% purity as judged by analytical gas chromatography on either a dimethylsulfolane or a β,β'-oxydipropionitrile column and by GC–MS. The major impurities were the other 2,4-hexadiene isomers. 1,3-Hexadiene was a mixture of cis and trans isomers which was only partially resolved on the β,β'-oxydipropionitrile column. Infrared absorption spectra in the 800–1100-cm^{-1} region are shown in Figure 1. The most intense absorptions are attributed to modes with significant vinyl out-of-plane deformations.[6] Samples were contained in 10-cm path length by 2.5-cm i.d. Pyrex cells fitted with NaCl entrance and exit windows. High-vacuum Kontes valves were used to connect to a vacuum line or the gas inlet system of a flame ionization gas chromatograph or GC–MS. Irradiation of samples in the 10-μ to 1-Torr region was carried out via the output of a Rogowski profile double discharge CO_2 TEA laser. Operation on either the R(18) or P(38) transition of the 10.6-μ laser branch was confirmed using a CO_2 laser spectrum analyzer. Output pulses were monitored with a photon drag detector and consisted of a sharp (60 ns) spike containing ~70% of the pulse energy followed by a low intensity tail of approximately 400-ns duration. An unfocused beam of ~1.2-cm diameter was employed with the beam profile being monitored periodically via burn patterns on heat sensitive paper. The energy of a single pulse as measured by a calibrated thermopile was 1.6 ± 0.1 J and 0.9 ± 0.1 J on R(18) and P(38), respectively. Satisfactory GC analysis was possible for sample pressures as low as 10 μ following single-pulse irradiation.

Product ratios obtained for single-pulse excitation of the