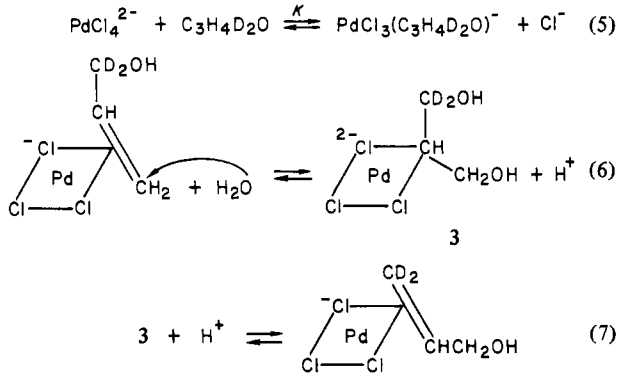
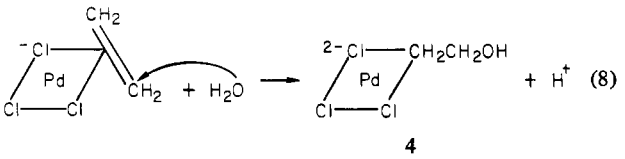


of Pd(II) for a cis attack would have required a square chloride inhibition.

Since allyl alcohol undergoes this trans attack of water to give **3**, it is almost certain that ethene also undergoes a similar hydroxypalladation to give **4** (eq 8) with a rate expression analogous to eq 4. Of course, in the case of ethene there would be no way



of detecting this type of hydroxypalladation unless the adduct, **4**, was intercepted by some reagent such as $CuCl_2$. The adduct **4** must therefore by considered as a possibility for the intermediate which is actually intercepted in the stereochemical studies using ethene-d_2. One experimental observation, in fact, strongly favors **4** as this intermediate. In the original studies[7] on chloroethanol formation it was found that high chloride concentration (ca. 5 M) *as well as* high cupric chloride concentration (ca. 4 M) was required for chloroethanol formation. If only cupric chloride is present the product was almost exclusively acetaldehyde. These results are *not* consistent with $CuCl_2$ intercepting the same intermediate, **1**, which decomposes to give acetaldehyde, but are consistent with repression of the acetaldehyde formation, which has a square chloride inhibition (eq 1), so that chloroethanol becomes the predominate reaction. This situation would only arise if chloroethanol formation does not have as strong a chloride inhibition as acetaldehyde formation. Chloroethanol formation, if it does proceed via **4**, would have only a first-order chloride inhibition and thus be strongly favored over acetaldehyde formation at high $[Cl^-]$. A reaction sequence consistent with these considerations is shown in Scheme III.[12] The trans stereochemistry observed for chloroethanol formation[4] is expected on the basis of this scheme. Thus the present results provide a plausible alternate reason for the stereochemistry observed in chloroethanol-d_2 formation. In any case the detection of the second mode of hydroxypalladation does demonstrate the hazards of interpreting stereochemical results in terms of kinetic results especially if the stereochemistry is not studied under the same conditions as the kinetics. Of course the choice between the two routes given by eq 2 and 3 cannot be made on the basis of the present results, but the question as to which is operative remains open.

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(12) The reason **1** decomposes to acetaldehyde while **4** does not could be that the cis H_2O ligand in **1** is more labile than the cis Cl^- ligand in **4**. The decomposition of **1** by hydride elimination has recently been discussed,[1,4] and the need for a vacant coordination site for hydride elimination has been indicated by kinetic studies.[13,14]

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Isotopic Labeling at Natural Abundance: Multiphoton Dissociation of Perfluoropropene†

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Experiments using molecules with isotopically labeled sites provide useful insight into reaction mechanisms by helping in the identification of transition states, locating centers of radical attack, and indicating routes of isomerizations.[1] The general use of this technique has been restricted in practical terms because the synthesis of substrates with specifically labeled sites is expensive and/or tedious. Infrared laser photolysis offers the potential that this technique can be applied much more generally since it allows isotope-labeled experiments with substrates at natural abundance. Multiphoton infrared excitation is isotopically selective, and by choosing which vibrational mode is activated, one may make the isotopic labeling specific to one site in the molecule. For example, irradiation to the red edge of the ν_{15} band of hexafluoroacetone activates only $CF_3{}^{13}COCF_3$ molecules.[2] This is because the ν_{15} vibration corresponds to an asymetric C-C-C stretch[3] which will have a small isotope shift for $^{13}CF_3COCF_3$ molecules. We report here the first example of the use of this technique to obtain significant information about the topology of a chemical reaction.

We illustrate the technique with results from the isotopically selective infrared multiphoton photolysis of carbon-13 substituted perfluoropropene, obtained by using natural abundance substrates. First reports of the gas-phase pyrolysis of the compound suggested that the primary dissociation step was a bond scission to yield C_2F_4 and CF_2.[4] Subsequently it was proposed that perfluorocyclopropane must be a precursor to dissocation,[5] and indeed this compound was observed in the single-pulse shock-tube pyrolysis of perfluoropropene.[6] We have investigated the infrared multiphoton dissociation of perfluoropropene, following irradiation with the P(28) line of the $^{12}CO_2$ laser at 1039 cm^{-1}. This line is close to the maximum of the strong infrared absorption band at 1037 cm^{-1}. Preliminary results establish the following simple kinetic mechanism:[7]

$$CF_3CFCF_2 \xrightarrow{nh\nu} C_2F_4 + CF_2 \quad (1)$$

$$CF_2 + CF_2 \rightarrow C_2F_4 \quad (2)$$

We have investigated the intermediacy of the cyclopropane intermediate in reaction 1 by performing irradiations on the red edge of the 1037-cm^{-1} band using the P(16) and P(26) lines of the $^{13}CO_2$ laser[8] at 1004 and 995 cm^{-1}, respectively.

Irradiations were performed with a parallel beam at 2 J cm^{-2} incident fluence and were carried to 10% conversion in the minor isotopic component. Following irradiation the product C_2F_4 was distilled from the substrate at -160 °C and analyzed by mass spectrometry. The $C_2F_3{}^+$ ion peaks at m/e 81, 82, and 83 were

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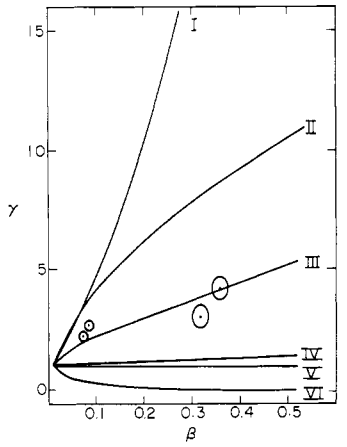

Figure 1. Relations between product isotopic abundance ratios β and γ (see text). The six curves are for all possible combinations of isotopically labeled sites (S) and leaving groups (L); S = 1, 2, and 3 and L = 1, 2, and 3 for CF_3, CF, and CF_2, respectively. There are many possible ways to generate each curve: typical examples are (I) S = 1, L = 2; (II) S = 1 + 2, L = 1 or 3; (III) S = 1, L = 1, 2, or 3; (IV) S = 1, L = 1 or 3; (V) S = 1, L = 1 + 2 + 3; (VI) S = 1, L = 1. The data points were obtained for 0.5-torr perfluoropropene following irradiation at 1004 cm^{-1} (small circles) and 995 cm^{-1} (large circles).

used to determine both the ratio of carbon-13 to carbon-12 in the products [$\beta = (2I^{83} + I^{82})/(2I^{81} + I^{82})$] and a suitably defined peak height distribution factor [$\gamma = (I^{82})^2/(4I^{81}I^{83})$].

The factors γ and β may be related through an intimate description of the reaction mechanism. In the present case this description is complicated as no normal coordinate analysis has been performed upon perfluoropropene,[9] and we are therefore unable to state unequivocally which specific site or sites are isotopically labeled. However, we shall see below that an analysis of the kinetics is not precluded by this lack of information. It would have been considerably simplified though if the assignment of the vibration had been made. We have proceeded by melding all possible combinations of selectively labeled site or sites with all possible combinations of leaving group or groups. There are then six possible relationships between γ and β for any value of the primary selectivity (we are able to vary this selectivity by making small changes to the irradiation frequency). These have been calculated and are displayed in Figure 1. To give a trivial example of this procedure: curve V corresponds to the unlikely mechanism $C_3F_6 \rightarrow 3CF_2$; in this case γ = 1, independent of labeled site and β. Fortunately, the experimental data points are consistent with only one of the six curves. This curve (III) is pertinent to either of two scenarios: either (i) all three carbon atoms have equivalent isotope shifts or (ii) all three carbon atoms are equally likely to provide the leaving group. We consider the first possibility to be unlikely, and the only reasonable transition state to support the second finding is the cyclic intermediate:

$$C_3F_6 \xrightarrow{nh\nu} [CF_3CFCF_2^* \rightleftharpoons [c\text{-}C_3F_6]] \rightarrow CF_2 + C_2F_4$$

We have demonstrated that isotopically selective laser-driven dissociation of natural abundance material can yield significant topological information. In the present case this information was gleaned in the absence of a precise normal coordinate description of the vibration excited, although such description would have further simplified the data analysis. Wide exploitation of this technique should be possible.

Supplementary Material Available: A full description of the reaction mechanisms considered and a detailed derivation of one of the curves in the figure (7 pages). Ordering information is given on any current masthead page.

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Hydroxide Ion as a Catalyst for Nucleophilic Substitution of Thiamin Analogues by Thiolate Ions. A Rival for Sulfite Ion

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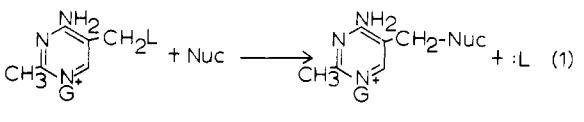
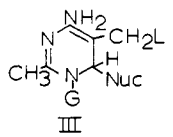
Nucleophilic substitution of thiamin (I, vitamin B_1) by sulfite ion to give sulfonate II (Nuc = SO_3^-) and a thiazole leaving group (L_1) (eq 1) is a characteristic reaction of the vitamin and is often regarded as unique. Only recently has a mechanism been established for this old reaction:[1] sulfite ion adds to protonated substrate to give one or more intermediates such as III (Nuc = SO_3^-, G = H) which then react with a second sulfite ion to lead to product.[2] Kinetic data show under special conditions the required second-order dependence on sulfite ion for thiamin[3] and also for a thiamin analogue.[4]

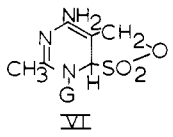


I: L_1, G=H
IV: L_2, G=CH_3
V: L_3, G=CH_3

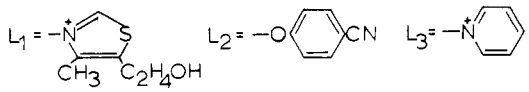
II



III



VI



We now report that hydroxide ion behaves much like sulfite ion when reacting with thiamin analogues. Both nucleophiles react by a similar mechanism.

Thiamin analogues IV and V contain *p*-cyanophenoxide ion and pyridine leaving groups, respectively. Both have a pyrimidine ring made electrophilic by quaternization.[5] In alkaline solution they undergo hydrolysis (eq 1). Spectrophotometrically obtained pseudo-first-order rate constants show a first-order dependence on hydroxide ion; there is no significant buffer catalysis (Table I). Thiamin under comparable conditions undergoes hydrolytic opening of its thiazolium ring[6-8] rather than substitution.

Hydrolysis products were established by using ^1H NMR. Leaving groups are easily identified. Comparison of chemical shifts with those for authentic II (Nuc = OH[9]) identifies the pyrimidine ring. The nature of the nucleophile attached to II is most interesting. When either substrate is hydrolyzed in a PO_4^{3-} buffer, a phosphate ester is formed (Nuc = OPO_3^{2-}), easily characterized by its 6.5-Hz coupling (δ 4.7) between the methylene

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