M sodium acetate containing undecane as an internal standard was heated at 75 °C for 18 h (22 half-lives). After the workup of the solution, GLC analysis showed that the amount of **11b** remained unchanged but **11d** underwent substantial isomerization (ca. 57%) to **11c**.[24]

Acknowledgment. We express appreciation to the National Science Foundation for support of this work with Grant CHE-76-01129.

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Infrared Laser Induced Organic Reactions. 2.[1] Laser vs. Thermal Inducement of Unimolecular and Hydrogen Bromide Catalyzed Bimolecular Dehydration of Alcohols

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Abstract: It has been demonstrated that a mixture of reactant molecules can be induced by pulsed infrared laser radiation to react *via* a route which is totally different from the pathway resulting from heating the mixture at 300 °C. The high-energy unimolecular elimination of H_2O from ethanol in the presence of 2-propanol and HBr can be selectively induced with a pulsed CO_2 laser in preference to either a lower energy bimolecular HBr-catalyzed dehydration or the more facile dehydration of 2-propanol. Heating the mixture resulted in the almost exclusive reaction of 2-propanol to produce propylene. It was demonstrated that the bimolecular ethanol + HBr reaction cannot be effectively induced by the infrared laser radiation as evidenced by the detrimental effect on the yield of ethylene as the HBr pressure was increased. The selective, nonthermal inducement of H_2O elimination from vibrationally excited ethanol in the presence of 2-propanol required relatively low reactant pressures. At higher pressures intermolecular V–V energy transfer allowed the thermally more facile dehydration from 2-propanol to become the predominant reaction channel.

There is currently much interest in the application of high-intensity, pulsed infrared lasers to induce or augment chemical reactions.[3] Excitation of a molecule with such a laser can result in the absorption of many infrared photons and promotion of the molecule to high vibrationally excited states. Most of the chemical systems investigated to date have involved

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unimolecular decompositions or rearrangements with only a relatively few simple bimolecular reactions having been studied.[4,5] Whereas vibrational excitation is known to be highly effective in promoting a unimolecular process, the effect of such excitation on a bimolecular reaction is less obvious. For various simple di- and triatomic systems, vibrational excitation of one of the reacting partners has been demonstrated to enhance, retard, or have no effect on the overall reaction kinetics.[4] In addition, collisional deactivation of the vibrationally excited molecule by the reacting partner is expected to be an important competing process, particularly for more complex organic molecules.[6]

In this paper we report the influence of intense, pulsed infrared laser radiation on the dehydration of ethanol and 2-propanol in the presence of HBr catalyst. The competitive use of two alcohols follows from our earlier work[1] and allows a distinction between a nonequilibrium laser process and simple heating by the laser. In the HBr-catalyzed bimolecular process[7] the HBr is both a reacting partner and a catalyst for the dehydration. The substantial reduction in activation energy effected by the HBr as compared to unimolecular dehydration was deemed an advantage which might allow the bimolecular process to more effectively compete with collisional deactivation.

We have observed different reaction channels resulting from infrared laser excitation of the reactants as compared to simple heating of mixtures of ethanol, 2-propanol, and HBr. At low pressures, pulsed, selective excitation of the ethanol resulted in the almost exclusive formation of ethylene via an unimolecular pathway in preference to the more facile uni- or HBr-catalyzed dehydration of 2-propanol. Heating a similar mixture resulted in the nearly exclusive formation of propylene via elimination from 2-propanol. The principal effect of the HBr in the laser reaction was not to catalyze the dehydration process but to collisionally deactivate the vibrationally excited alcohol.

Experimental Section

Ethanol and 2-propanol were commercially available and distilled before use; vapor-phase chromatography of the middle fractions showed no impurities. The HBr was supplied by Matheson and used without further purification.

All infrared laser irradiations were performed with a Lumonics Model 203 CO_2 laser. The P(28) line of the 001-020 transition (1039.37 cm^{-1}) was utilized for excitation of ethanol. Irradiation with the P(14) line of the 001-100 transition (949.48 cm^{-1}) selectively excited 2-propanol. Partial focusing of the laser beam was achieved with a 50-cm focal length BaF_2 lens; the sample was positioned 20 cm from the lens to produce a fluence of 3.0 J/cm^2 in the center of the cell. Typically, samples were pulsed 25-200 times; the lower the reactant pressure, the more pulses were required to produce sufficient quantities of products for analysis. Infrared spectroscopy and vapor phase chromatography showed that pulsed irradiation of ethanol produced ethylene and acetaldehyde as the only significant organic products.[8]

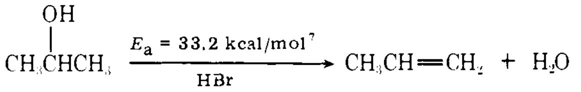
Samples for laser irradiation were prepared by standard vacuum-line techniques and contained within 10 × 2.0 cm diameter Pyrex cells fitted with NaCl windows. Heated samples were contained in 15 cm × 16 mm diameter Pyrex tubes equipped with a Teflon valve and Viton O-ring. The tubes were uniformly wrapped with heating tape and then insulated. The desired operating temperature could be reached within 2 min and maintained within ±5 °C.

Analyses of ethylene and propylene were performed with a Varian Model 2700 gas chromatograph equipped with a flame ionization detector. A 20 ft × $\frac{1}{4}$ in. 30% propylene carbonate column followed by a 5 ft × $\frac{1}{8}$ in. 10% Carbowax 20M column was used at ambient temperature. A correction for the detector response was applied to the ethylene and propylene peak areas.

Results and Discussion

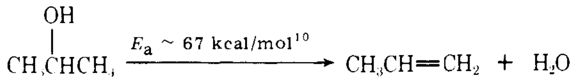
The gas-phase HBr-catalyzed dehydrations of ethanol (eq 1) and 2-propanol (eq 2) have been shown[7] to occur at much lower temperatures than the uncatalyzed processes (eq 3 and 4) in accordance with the approximately 35 kcal/mol differences in activation energies.

$$CH_3CH_2OH \xrightarrow[HBr]{E_a = 37.6\ kcal/mol^{9}} CH_2{=}CH_2 + H_2O \qquad (1)$$



$$CH_3CH(OH)CH_3 \xrightarrow[HBr]{E_a = 33.2\ kcal/mol^{7}} CH_3CH{=}CH_2 + H_2O \qquad (2)$$

$$CH_3CH_2OH \xrightarrow{E_a \sim 71\ kcal/mol^{10}} CH_2{=}CH_2 + H_2O \qquad (3)$$



$$CH_3CH(OH)CH_3 \xrightarrow{E_a \sim 67\ kcal/mol^{10}} CH_3CH{=}CH_2 + H_2O \qquad (4)$$

Reaction 2 has a rate constant of $k_2 = 10^{12.0} \exp(-33\,200/RT)\ s^{-1}\ cm^3\ mol^{-1}$; reaction 1 has been reported to be approximately 20 times slower than reaction 2 at 472 °C.[7] The uncatalyzed unimolecular reactions are less well characterized and the activation energies indicated were estimated from 2-methyl-2-propanol data.[10] The precise values of E_a for reactions 3 and 4 are not required for the present discussion.

The following experimental results are pertinent:

(1) Irradiating ethanol in a 1.0:1.0:0.5 mixture of ethanol-2-propanol-HBr produced varying ratios of ethylene: propylene depending upon the total reactant pressure as depicted in Figure 1.

(2) Irradiating ethanol in a 1.0:1.0 mixture of ethanol and 2-propanol (without HBr) produced ethylene:propylene ratios similar to those of Figure 1.

(3) Heating a mixture with initial pressures of 0.5 Torr ethanol, 0.5 Torr 2-propanol, and 0.25 Torr HBr at 300 °C for 20 min produced a mixture of >98% propylene and <2% ethylene. Without HBr a similar ratio was observed but the addition of HBr significantly catalyzed the reaction, as expected.[7]

(4) Irradiation of 2-propanol in a mixture of 0.1 Torr 2-propanol and 0.1 Torr ethanol yielded a mixture of 92% propylene and 8% ethylene.

(5) The detrimental effect of HBr on the yield of ethylene from the irradiation of 0.5 Torr of ethanol is shown in Figure 2.

It is evident from results 1 and 3 that the laser-induced reaction of a mixture of ethanol, 2-propanol, and HBr takes a completely different course as compared to simply heating the same mixture at 300 °C. Irradiation of ethanol in the mixture produces almost exclusive unimolecular formation of ethylene provided that the total pressure is relatively low (Figure 1). Heating such a mixture results in >98% formation of propylene with essentially no ethylene produced. It is obvious that the laser selectively activates ethanol to sufficiently high vibrational levels that either reaction 1 or 3 occurs provided that the total reactant pressure is kept low. Under these conditions, laser-induced, nonthermal, nonequilibrium chemistry occurs. The lower E_a for unimolecular dehydration of 2-propanol and similar A factors for both alcohols would require that propylene be the predominant product under all thermally equilibrated conditions. At higher pressures, V-V and V-T,R intermolecular energy transfer to 2-propanol indeed takes place and dehydration of this alcohol with the lower E_a occurs. When the requisite energy is supplied by random heating (result 3), the preferred reaction pathway is formation of propylene. Moreover, laser excitation of 2-propanol in the presence of ethanol results in almost exclusive reaction of the former (result 4).

It is important to note that the thermal behavior of these

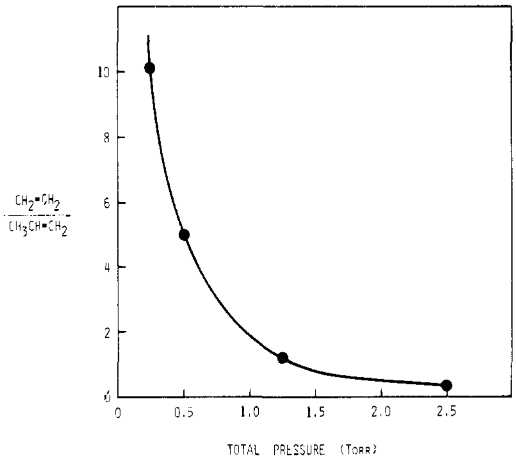


Figure 1. Ethylene/propylene ratios as a function of total reactant pressure in 1.0:1.0:0.5 mixtures of ethanol, 2-propanol, and HBr. Laser pumping at 1039.37 cm^{-1} and 3.0 J/cm^2 selectively excited the ethanol.

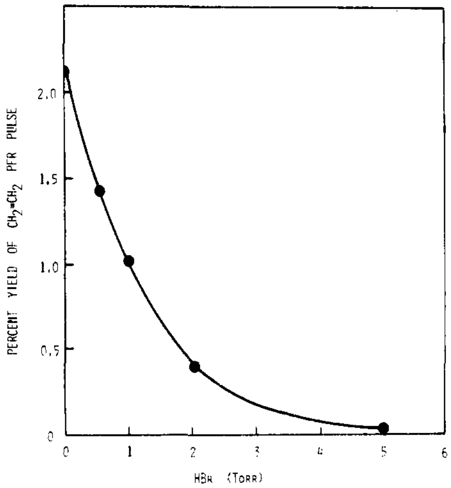


Figure 2. Percent yield of ethylene produced in the irradiated volume per laser pulse from 0.50 Torr of ethanol as a function of HBr pressure; laser fluence = 3.0 J/cm^2.

systems is expected to be different at 300 °C as compared to the effective vibrational temperatures reached during laser excitation. The latter are estimated to be quite high, probably in the range 1000-2500 °C.[13] The lower A factors for the bimolecular HBr-catalyzed processes would predict reaction via these channels to become less important relative to unimolecular dehydration but to still predominant even at such high effective vibrational temperatures.

That the laser is promoting the unimolecular elimination of H_2O from ethanol (reaction 3 rather than reaction 1) is apparent from the consideration of results 2 and 5. These demonstrate that HBr has no significant effect on the ethylene:propylene ratio and a detrimental effect on the yield of ethylene per pulse (Figure 2). This latter point is particularly significant. Unlike conventional thermally promoted bimolecular reactions in which increasing the concentration of one of the reactants results in a concomitant rate increase, in the laser-induced elimination of H_2O from ethanol the yield of ethylene is actually diminished by an increase in the concentration of HBr. This observation is easily rationalized. By definition, in a bimolecular process two reactants must collide. The collision may lead to reaction but for a relatively large, vibrationally excited, polyatomic molecule such as ethanol colliding with a polar reagent such as HBr, it is anticipated that the V-V relaxation rate will be rapid (≥ 0.1 of the gas kinetic collision frequency).[1,6] Therefore, the HBr is more effective as a heat sink than it is as a catalyst for the dehydration reaction.

Collisional deactivation by the nonexcited reaction partner may be a general result for an infrared laser induced bimolecular reaction involving even moderate-sized organic molecules, particularly if the reaction has a low Arrhenius A factor and if relative translational energy is required to overcome the activation barrier. A similar observation in which the probability of vibrational deactivation is higher than the probability of chemical reaction was noted in the reaction of SF_6 with hydrogen halides.[14] In contrast, Gupta, Karny, and Zare have preliminary evidence suggesting that the pulsed infrared laser induced unimolecular isomerization of cyclopropane might be enhanced by adding HBr, BBr_3, or BCl_3; the laser isomerization of *cis*- or *trans*-1,2-dimethylcyclopropane responded only to HBr as a catalyst.[15] Although the reason(s) for the differences between the laser-induced HBr-catalyzed isomerization of cyclopropanes and the HBr-catalyzed dehydration of alcohols described in the present work are not obvious, it is noteworthy that cyclopropane is a much more rigid molecule than ethanol and not as prone to undergo V-V and V-T,R transfer at least from low vibrational excitation levels.[6] The observations reported herein in which collisional deactivation competes effectively with the bimolecular reaction channel will probably be a more general result for infrared laser induced reactions of organic molecules.

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Infrared Spectrum of the Intramolecular Hydrogen-Bonded Chloroform Anion Cl^-–$HCCl_2$ in Solid Argon at 15 K

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Abstract: The matrix photoionization products of chloroform, including its deuterium and ^{13}C isotopes, and the $CHCl_2Br$ and $CHCl_2I$ compounds have been studied by infrared spectroscopy. The anion product exhibits isotopic data appropriate for a single H, single C, and two equivalent Cl atom species, while bromine and iodine substitution data indicate the involvement of a third inequivalent halogen atom; these observations identify the Cl^-–$HCCl_2$ anion, which is produced upon electron capture by chloroform. The infrared spectrum containing ν_s, $2\nu_b$, ν_b, and ν_x clearly demonstrates the effect of hydrogen bonding in Cl^-–$HCCl_2$, which decreases in the Br^-–$HCCl_2$ and I^-–$HCCl_2$ anions.

Introduction

Thermal electron capture by chloromethanes in the gas phase is generally considered to be a dissociative process giving chloride ion and the appropriate methyl radical. The intermediate parent radical anion in this process is of limited stability since the radical anion electron probably first occupies a σ^*(C–Cl) antibonding orbital and this C–Cl bond is easily dissociated. Direct spectroscopic evidence for parent radical anions of this type is limited to recent ESR studies of CF_3Cl^-, $CF_2Cl_2^-$, and $CFCl_3^-$ following γ-radiolysis of the parent in tetramethylsilane at 101 K,[1] to infrared detection of $CHCl_3^-$ and $CHBr_3^-$ prepared by proton radiolysis of the haloforms during condensation with excess argon at 15 K,[2] and to infrared observation of CF_3Cl^-, CF_3Br^-, and CF_3I^- and the possible infrared detection of $CF_2Cl_2^-$ and $CFCl_3^-$ following argon resonance photoionization of the precursors during condensation with argon at 15 K.[3,4]

The $CHCl_3^-$ radical anion in solid argon readily photodissociated, but the products were not identified.[2] Since hydrogen bonding has been documented for chloroform,[5] the possibility of an intramolecular hydrogen-bonded chloroform anion must be considered for the decomposition product of $CHCl_3^-$ in condensed media. Three infrared matrix isolation studies involving electron capture by chloroform have been reported, but the stable anion product was identified as $CHCl_2^-$ in each case.[6,2,7] We report here a reinvestigation of the chloroform electron capture product, including infrared studies on the bromine and iodine substituted compounds, with a reassignment of the infrared absorptions to the intramolecular hydrogen-bonded anion Cl^-HCCl_2, which is of considerable chemical and spectroscopic interest as a model compound for hydrogen bonding.

Experimental Section

The experimental methods and apparatus have been described in detail elsewhere.[8-10] Samples of chloroform ($CHCl_3$, $CDCl_3$, and $^{13}CHCl_3$), dichlorobromomethane, and dichloroiodomethane in argon (Ar/CHX_3 = 400/1) were condensed on a CsI window at 15 K and simultaneously exposed to an open argon microwave discharge through a 1-mm orifice for 20-h periods. Dichloroiodomethane was synthesized by the reaction of iodoform and mercuric chloride.[11] The solid compounds (10 g of CHI_3 and 14 g of $HgCl_2$) were ground together, placed in a Pyrex tube attached to a vacuum line, and heated to about 95 °C. Dichloroiodomethane was distilled into a cold finger; the liquid product was faint purple owing to the presence of iodine impurity. The matrix sample was prepared by distilling $CHCl_2I$ from $Mg(ClO_4)_2$; infrared spectra showed about 5% $CHCl_3$ impurity. A Beckman IR-12 infrared spectrophotometer was used to record spectra at 8 cm^{-1}/min on expanded wavenumber scale before and after filtered high-pressure mercury arc photolysis of these matrix samples; wavenumber accuracy is ±0.3 cm^{-1} when reported to the nearest 0.1 cm^{-1} and ±1 cm^{-1} otherwise.

Results

The infrared spectrum from a $CHCl_3$ experiment is illustrated in Figure 1a. The major product bands at 2723, 2499, 1291, and 1271 cm^{-1}, a triplet at 1038, 1035, and 1032 cm^{-1}, and a doublet at 838 and 836 cm^{-1}, labeled A and C in the figure, are in agreement with the earlier work of Jacox and Milligan (JM).[6,7] Using a 90% carbon-13 enriched $^{13}CHCl_3$ sample, the spectrum in Figure 2a was produced. The carbon-13 product bands shifted to 2714, 2493, 1282, and 1268 cm^{-1}, a triplet at 1013, 1010, and 1007 cm^{-1}, and a doublet at 813 and 811 cm^{-1}, also labeled A and C in the figure; the latter five bands are in agreement with JM, who could not resolve the former broad band into isotopic components with a 55% $^{13}CHCl_3$ sample. The absorption bands and intensities from this 90% ^{13}C experiment are listed in Table I; the observation of both ^{12}C and ^{13}C counterparts of the major product bands with 1:9 relative intensities indicates that the products are single carbon atom species.

High-pressure mercury arc photolysis of the 90% $^{13}CHCl_3$ matrix sample is of particular interest, and the spectra are contrasted in Figure 2. As seen in trace (b), 30 min of 290–1000-nm photolysis had little effect on the C bands, but the A absorptions were decreased by 60%, broad 705- and 974-cm^{-1} bands were markedly increased, and a comparatively sharp 3:1 relative intensity 898.0–891.7-cm^{-1} doublet appeared in the spectrum. The sample was next exposed to the water-filtered arc (220–1000 nm) for 30 min, and the resulting spectrum is shown in Figure 2c; the C bands were reduced by 40%, the A absorptions were slightly increased, while the 974-, 898-, 892-, and 705-cm^{-1} bands were decreased. A final exposure to the water-filtered arc for an additional 100 min reduced all of the

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