are due to the oxygen atoms of disordered [$H^+{\cdot}nH_2O$] ions. At least one of these ions (an $H_5O_2^+$ ion) is *not* disordered yielding reasonable thermal parameters and an O(1)–O(1) hydrogen bonded distance of 2.45 (5) Å, similar to those found in other structures containing this ion.[16] Hydrogen bonds are formed between this ion and Cl(1D) [3.20 (2) Å] and Cl(2A) [2.99 (2) Å]. Partially occupied oxygen atoms [O(2) and O(3)] were also placed from difference Fourier maps, their positional and thermal parameters refined with their occupancy factors fixed at 0.5. Reasonable temperature factors were obtained in this way, but full confidence cannot be placed on the values for the parameters of these atoms. In spite of the difficulties arising from the disordering problem of the [$H^+{\cdot}nH_2O$] ions, the reasonable values obtained for the Rh–Rh bond distances and the overwhelming chemical evidence[4,8] give us confidence that the formal oxidation level is indeed 1½ for each of the four Rh atoms in the tetranuclear unit, giving an overall charge of +5 to the $Rh_4(bridge)_8Cl^{5+}$ unit. This requires the formula to be $H_3[Rh_4(bridge)_8Cl](CoCl_4)_4{\cdot}nH_2O$, where *n* is at least 3 and more likely 6.

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Supplementary Material Available: Final atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(8) The infrared spectra of model rhodium isocyanide complexes in the $\bar{\nu}$(CN) region are as follows: Rh(I) complexes, $[Rh(CN\text{-}t\text{-}Bu)_4]Cl$, 2164 cm^{-1} (KBr pellet)[6] and $Rh_2(bridge)_4(BPh_4)_2{\cdot}CH_3CN$, 2172 cm^{-1} (KBr pellet);[7] binuclear Rh(II) complexes, $[Rh_2(bridge)_4Cl_2]Cl_2$, 2246 cm^{-1} (Nujol mull), and $[Rh_2(bridge)_4I_2](I_3)_2$, 2227 cm^{-1} (KBr pellet);[7] Rh(III) complexes, $[Rh(CN\text{-}i\text{-}Pr)_4Cl_2](PF_6)$, 2250 cm^{-1} (KBr pellet),[6] and $[Rh(CNCH_3)_4Cl_2](PF_6)$, 2280 cm^{-1} (KBr pellet).[6] These data suggest a rough correlation of the formal oxidation state of the Rh atoms with the position of $\bar{\nu}$(CN). Consistent with this correlation, $H_3[Rh_4(bridge)_8Cl][CoCl_4]_4{\cdot}nH_2O$, which formally contains Rh(I½), shows a $\bar{\nu}$(CN) at 2221 cm^{-1} (Nujol mull) and a weak shoulder to the higher energy side of the band, placing it between the Rh(I) and Rh(II) model complexes. A dark blue ClO_4^- salt obtained by addition of $NaClO_4$ to blue aqueous HBr solutions of $Rh_2(bridge)_4(BF_4)_2$ analyzes for $Rh_2(bridge)_4(ClO_4)_3$. Calcd: C, 20.34; H, 2.22; N, 9.49; Cl, 18.01. Found: C, 20.41; H, 2.57; N, 9.47; Cl, 17.97. This salt also shows a $\bar{\nu}$(CN) region (2228 cm^{-1}, weak shoulder to higher energy, Nujol mull) virtually identical with that found for $H_3[Rh_4(bridge)_8Cl][CoCl_4]_4{\cdot}nH_2O$.

(9) The Cl^- binding constant determined in aqueous 0.1 M HSO_3CH_3 by making plots of the equation $\log\{[Rh_4(bridge)_8Cl_n]^{(6-n)+}/[Rh_4\,(bridge)_8{}^{6+}]\} = \log K + n \log [Cl^-]$ gives $n = 1.0 \pm 0.1$, and $\log K = 2.8 \pm 0.2$ at 25 ± 1 °C, maximum $[Cl^-] = 0.01$ M. Binding of an additional Cl^- at the high $[Cl^-]$ present in 12 M HCl solutions is also likely to occur.

(10) The strong visible absorption band ($\lambda_{max} \approx 558$ nm) exhibited by $Rh_4(bridge)_8Cl^{5+}$ in 12 M HCl solution, upon cooling, shows the characteristic hypsochromic shift and increase in ϵ_{max} associated with the $\sigma \rightarrow \sigma^*$ transitions found in compounds which contain single metal–metal bonds. See Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975,** *97*, 6042–6047. The extremely low position energetically for this transition must at least in part be due to delocalization of the transition over all four Rh atoms.

(11) Crystals of this complex were obtained with extreme difficulty. Evaporation of the 12 M HCl solution was carried out in a desiccator in which were placed a beaker of P_2O_5 (to remove H_2O) and a beaker of NaOH pellets (to remove HCl). The solutions are slowly air and light sensitive. The green crystals obtained become opaque *seconds* after removal from the mother liquor. Most of the crystals in a batch grow as flat crosses. The crystal used in this study was mounted in a capillary in a minimally lighted room by transferring a crystal in constant contact with the mother liquor to the wide end of the capillary which was also opened at the opposite end. The crystal was then forced into the capillary until it wedged by causing mother liquid to flow through the capillary. Both ends of the capillary were then sealed with epoxy. Once mounted in this way, the crystal was stable, mechanically and chemically, as evidenced by the lack of observable movement or decomposition during the data collection. Density measurements (flotation in CCl_4–1,1,2,2-tetrabromoethane) depend on how long the crystals have been removed from the mother liquor. For crystals removed for longer than 1 week $\rho_{obsd} = 1.79$ (1) g cm^{-3}; for crystals taken directly from the mother liquor, $\rho_{obsd} = 1.7$ (1) g cm^{-3}; during this measurement (~10 min) the crystals had also become opaque, probably with solvent loss. ρ_{calcd} for $Z = 2$, $H_3[Rh_4(bridge)_8Cl](CoCl_4)_4{\cdot}6H_2O$, = 1.626 g cm^{-3}.

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Selective Enhancement of Bimolecular Reaction Rates by Over Three Orders of Magnitude Using Low Intensity CW Infrared Laser Radiation

Sir:

Chemists are understandably intrigued by the possibility of selective *unimolecular* dissociation processes using pulsed high power infrared lasers.[1] The fervor in this field somewhat overshadows the equally interesting possibility of utilizing infrared lasers to selectively modify *bimolecular* reaction rates.[2] We report here the use of a relatively low power (34 W/cm²) CW infrared laser to increase selectively the rate constant of a single bimolecular reaction by three orders of magnitude in a complex system, thus achieving a situation which is distinctly nonthermal. The reacting species are gas-phase ions which are generated, stored for periods up to 1 s, and detected using the techniques of ion cyclotron resonance (ICR) spectroscopy. Full details of ICR spectroscopy,[3,4] including modifications for infrared photochemistry,[5] are published elsewhere.

The equilibrium

$$(CH_3OH)H^+(OH_2) + CH_3OH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CH_3OH)_2H^+ + H_2O \quad (1)$$

is characterized by forward rate constant $k_f = 5.0 \times 10^{-10}$ cm³ mol^{-1} s^{-1} and reverse rate constant $k_r = 8.2 \times 10^{-15}$ cm³ mol^{-1} s^{-1}. k_f is measured using ICR techniques, whereas k_r is calculated from k_f and the equilibrium constant K. The value $\Delta G = -6.5 \pm 1.0$ kcal/mol[6,7] for reaction 1 gives $K = 6.1 \times 10^4$ in favor of proton-bound methanol dimer, $(CH_3OH)_2H^+$, at room temperature.

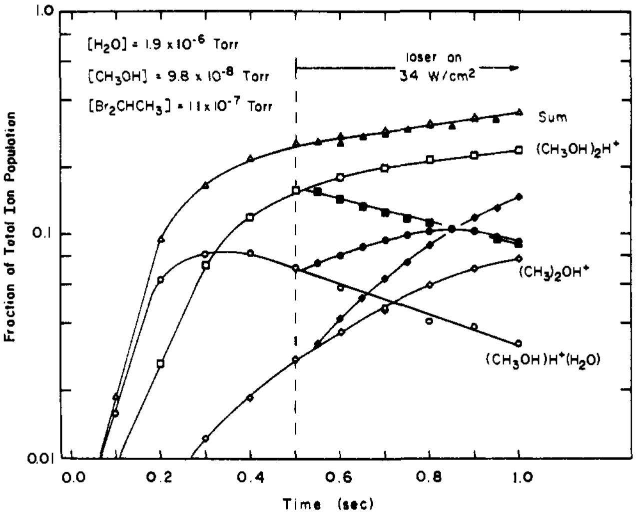

Figure 1. Variation of ion abundance with trapping time for the key ions derived from a mixture 1.9 × 10^{-6} Torr of H_2O, 9.8 × 10^{-8} Torr of CH_3OH, and 1.1 × 10^{-7} Torr of Br_2CHCH_3. Open symbols indicate unperturbed $(CH_3OH)_2H^+$ (□), $(CH_3)_2OH^+$ (◇), and $(CH_3OH)H^+(H_2O)$ (○), and filled symbols are ion intensities during CW laser irradiation (34 W/cm^2 at 947 cm^{-1}) beginning at 0.5-s trapping time. Triangles indicate sum of the three ion intensities with (▲) and without (△) laser irradiation. Ions are formed by a 70-eV, 10-ms electron beam pulse.

During CW laser irradiation ($\bar{\nu}$ = 947 cm^{-1}) at 34 W/cm^2, the reverse reaction rate is enhanced by more than three orders of magnitude to $k_r^{IR} = 2.6 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}. ICR double resonance[3,8] shows that the forward reaction is unaffected by laser irradiation.[9] In addition to the infrared-driven bimolecular reaction, the proton-bound methanol dimer undergoes multiphoton excitation followed by unimolecular decomposition:

$$(CH_3OH)_2H^+ \xrightarrow[nh\nu]{} (CH_3)_2OH^+ + H_2O \qquad (2)$$

The reaction endothermicity, ΔH = 17 kcal/mol[6,7] (corresponding to seven infrared photons absorbed), represents the *minimum* energy needed for process 2. At a total energy of 33 ± 1 kcal/mol, $(CH_3OH)_2H^+$ dissociates to $CH_3OH_2^+$ and CH_3OH.[6,7] Failure to observe this process indicates that reaction 2 requires <33 kcal/mol of excitation.

At the pressures (<10^{-5} Torr) and ion trapping times (up to 1 s) used in these experiments, the proton-bound methanol dimer is not produced in pure methanol.[7] A recently identified sequence of bimolecular reactions in a mixture of Br_2CHCH_3 and H_2O yields the proton-bound dimer of water.[10] Sequential displacement of water from $(H_2O)_2H^+$ by methanol yields the proton-bound dimer of methanol:

$$(H_2O)_2H^+ + CH_3OH \rightarrow (CH_3OH)H^+(OH_2) + H_2O \qquad (3)$$

$$(CH_3OH)H^+(OH_2) + CH_3OH \xrightarrow{k_f} (CH_3OH)_2H^+ + H_2O \qquad (4)$$

Other reactions occur to form $CH_3OH_2^+$ and $(CH_3)_2OH^+$ (processes 5 and 6). Details of the ion-molecule chemistry are given elsewhere.[10]

$$H_3O^+ + CH_3OH \rightarrow CH_3OH_2^+ + H_2O \qquad (5)$$

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \qquad (6)$$

Figure 1 shows the temporal variation of ion abundance for those species involved in both bimolecular and unimolecular infrared-driven reactions 1 and 2. The other ions in the system are omitted for clarity. Open symbols indicate normalized intensities of $(CH_3OH)_2H^+$, $(CH_3OH)H^+(OH_2)$, and $(CH_3)_2OH^+$ in the unperturbed system. Irradiation beginning at 0.5 s of trapping time alters the intensities of the three ions as indicated by the filled symbols. All other ions present are unaffected by laser radiation. Also shown in Figure 1 are the summed intensities of $(CH_3OH)_2H^+$, $(CH_3OH)H^+(OH_2)$, and $(CH_3)_2OH^+$, both with (▲) and without (△) laser irradiation. Invariance of the summed intensities to irradiation indicates these three ions are the only reactants and products of the infrared-driven reactions.

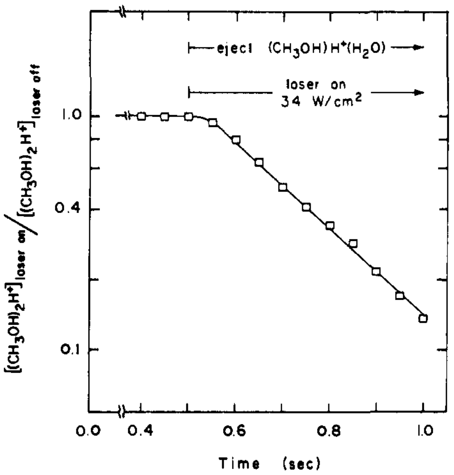

Figure 2. Semilog plot of fractional ion abundance vs. trapping time for laser induced reaction of $(CH_3OH)_2H^+$. Both double resonance ejection of $(CH_3OH)H^+(OH_2)$ and laser irradiation begin at 0.5 s. Neutral pressures and laser parameters are the same as in Figure 1.

Equations 7 and 8 govern the temporal abundance of the species of interest in this system:

$$\frac{d[(CH_3OH)_2H^+]}{dt} = -k_u[(CH_3OH)_2H^+] - k_r^{IR}[(CH_3OH)_2H^+][H_2O] + k_f[(CH_3OH)H^+(OH_2)][CH_3OH] \qquad (7)$$

$$\frac{d[(CH_3OH)H^+(OH_2)]}{dt} = -k_f[(CH_3OH)H^+(OH_2)][CH_3OH] + k_r^{IR}[(CH_3OH)_2H^+][H_2O] \qquad (8)$$

At 0.5 s of trapping time, when laser irradiation starts, reaction 3 has gone to completion and so is not included in eq 8. In Figure 1, the curve drawn through (laser on) data points for $(CH_3OH)H^+(OH_2)$ exhibits a maximum at ~850 ms. At the maximum, $d[(CH_3OH)H^+(OH_2)]/dt = 0$ and k_r^{IR} can be evaluated using eq 8 where the ion intensities are measured at 850 ms. Substitution of the measured quantities in eq 8 gives $k_r^{IR} = 2.6 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}.

In a second experiment ICR double resonance was used to eject $(CH_3OH)H^+(OH_2)$ beginning at 0.5 s of trapping time. The time scale for ejection is short compared with the time between collisions.[4,8] This reduces the concentration of $(CH_3OH)H^+(OH_2)$ to zero and prevents further formation of $(CH_3OH)_2H^+$ (reaction 4). Equation 7 is now modified since the third term on the right-hand side becomes zero, predicting laser-induced decomposition of $(CH_3OH)_2H^+$ to be pseudo first order (in dimer concentration) with an observed rate $k_{obsd} = k_u + k_r^{IR}[H_2O]$. Figure 2 shows a semilog plot of fractional $(CH_3OH)_2H^+$ abundance (defined as the ratio of ion intensity with the laser on to the signal intensity with the laser off) as a function of trapping time when both ejection of $(CH_3OH)H^+(OH_2)$ and laser irradiation begin at 0.5 s. Decomposition is first order as predicted, with the negative of the slope of the straight line in Figure 2 equal to k_{obsd} = 4.2 s^{-1}.

Thus, $k_u = 2.6\ s^{-1}$. For the laser power and neutral gas pressures used, the unimolecular decomposition is favored over the laser-driven bimolecular reaction by a factor of 1.6:1.

Both the forward and backward reactions in equilibrium 1 proceed through a common intermediate, $(CH_3OH)_2H^+(OH_2)$.[11] The competitive dissocation of this species is evaluated using RRKM theory,[12-14] where the internal energy is taken as absorbed infrared energy added to a 300 K Boltzmann distribution of vibrational energy. At an added energy of 10.5 kcal/mol the *calculated* ratio of H_2O to CH_3OH loss is equal to the observed value of $k_f/k_r^{IR} = 19.8$. This implies $(CH_3OH)_2H^+$ absorbs an average of 3.9 infrared photons ($\bar{\nu} = 947\ cm^{-1}$) prior to bimolecular reaction with H_2O.

Selective excitation of reactants not only represents an interesting tool for experimental chemical dynamics, it offers the possibility of using measured changes in reaction rates as a spectroscopic probe. The use of infrared excitation to alter bimolecular reaction rates should provide a general technique for obtaining vibrational spectra of ions and transient molecules.

Acknowledgment. We thank Professor R. Marcus for helpful discussions. This work was supported by the U.S. Department of Energy.

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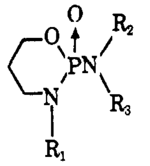
Resolution of Chiral Phosphamides

Sir:

The observation that the (−)-*S* isomer of cyclophosphamide {2-[bis(2-chloroethyl)amino]-2-oxo-1,3,2-oxazaphosphorinane, **1a**} is more effective against PC6 mouse tumors than the racemic mixture resulted in the development of a number of synthetic methods leading to the optically active forms of **1** and related compounds. Thus, the enantiomers of **1** were obtained by the separation of the diastereomers based on the additional optically active center introduced in the starting amino alcohol[2] or directly in **1**, using optically active naphthylphenylmethylsilyl chloride.[3] Following the resolution of isophosphamide[4] (**2**), an interesting synthesis of the enantiomers of triphosphamide (**3**) was recently published,[5] thus completing the picture. All of these methods except one[3] involve multistep asymmetric synthetic processes and are not direct methods for resolution of **1-3**.



	R_1	R_2	R_3
1	H	$-CH_2CH_2Cl$	$-CH_2CH_2Cl$
2	$-CH_2CH_2Cl$	H	$-CH_2CH_2Cl$
3	$-CH_2CH_2Cl$	$-CH_2CH_2Cl$	$-CH_2CH_2Cl$

Possibly the simplest way to resolve **1** would involve separation of complexes formed with optically active H donors. Based on the observation that **1a** forms a stable crystalline monohydrate,[6] it was expected that crystalline complexes with other H-bonding agents (alcohols, phenols) would be formed. No crystalline complexes of the anhydrous **1** were, however, obtained under various conditions,[7] using (+)-ethyl lactate, (+)-phenylephrine, (+)-quinine, or the optically active 1-(dimethylamino)ethanol or its *N*-oxide, or with the more acidic 1-trichloromethylethanol and 2-(α-hydroxyethyl)-4-nitrophenol. It is interesting to note that neither the pure *S* nor the *R* forms of **1** form monohydrate,[8] only the racemic mixture.

Here we report the optical resolution of the chiral phosphamide of the type **1** via its diastereomers of *N*-acyloxyalkyl type, as outlined in Scheme I. Thus, cyclophosphamide, (±)-**1**, can be transformed to the alkylol derivative **4**, by dissolving anhydrous **1** in chloral. After reacting them at room temperature overnight, the chloral excess was evaporated. The oily product was purified by chromatography on silica gel ($CHCl_3$–acetone, 9:1) and recrystallized from cyclohexane to give **4** in 50% yield: mp 125-128 °C; ^1H NMR ($CDCl_3$) δ 7.5 (d, 1 H exchangeable in D_2O), 5.5 (m, 1 H), 4.3 (m, 2 H), 3.6 (m, 10 H), 2.1 (m, 2 H) ppm. The obtained racemic **4** was

0002-7863/80/1502-3969$01.00/0