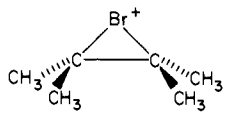

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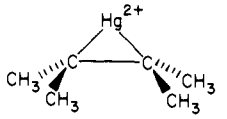

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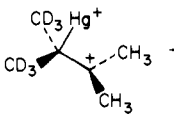
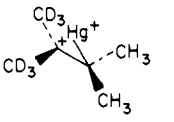
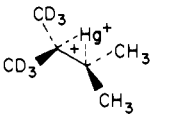


2a



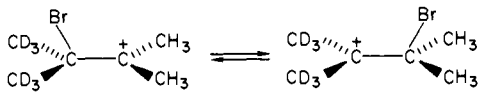
2b



10

and **2**[10,11] and also for the related compounds **3–6**, The results are summarized in Table I.[12] The two-bond isotope effect, $^2\Delta C(D)$, for **3–6** are small and shielding and are in the normal range of values reported for simple aliphatic molecules.[13] For **1**, the positive β-isotope effect ($^2\Delta C(D) = +1.5$ ppm) is somewhat larger than the value ($^2\Delta C(D) = +0.8$ ppm) observed for the *tert*-butyl-d_6 cation.[4a] For **2**, the β-isotope shift ($^2\Delta C(D) = -1.6$ ppm) and the γ-isotope shift ($^3\Delta C(D) = +1.5$ ppm) are highly unusual.

The large positive value of $^2\Delta C(D)$ for **1** cannot be due to an equilibrium isotope effect of the type **1a** ⇄ **1b**. An equilibrium



1a 1b

isotope effect would be expected to be temperature-dependent;[1] the isotope effect for **1** is independent of temperature over the range −63 to −33 °C. Furthermore, the equilibrium isotope effect for **1** would be expected to be negative since isotopic substitution will selectively destabilize **1b**. The results indicate that **1** has an electronic structure that responds to deuterium substitution in the same way as does a classical carbocation. The value of $^2\Delta C(D)$ of 0.75 ppm per CD_3 group indicates a strong hyperconjugative interaction with an electron-deficient p orbital at the 2-carbon in **1**. The bromonium ion appears to be best represented by a three-membered cyclic structure in which all bonds are of the two-electron two-center type.[14]

The negative value of $^2\Delta C(D)$ in the mercurinium ion **2** suggests that this ion has an electronic structure that responds to deuterium substitution in an entirely different way. The β-isotope effects in the 2-methyl-2-norbornyl **7**, 7-methyl-2-norbornen-7-yl **8**, and 1-methyl-1-cyclobutyl **9** cations are also negative and of comparable magnitude to that in **2**. In these cases the isotope shifts were attributed to the redistribution of the bonding electrons in a delocalized three-center, two-electron bond. The bonding in the mercurinium ion can also be described by a three-center, two-electron bond composed of a vacant orbital of Hg^{2+} and the 2p orbitals of the C2 and C3 carbons.

The absence of a temperature dependence of the isotope effect over the range from −63 to −33 °C and the similarity to the values for **7–9** suggest an isotopic perturbation of resonance rather than a perturbation of equilibrium. Because of the reduced hyperconjugative ability of the C–D bond, the preferred contributor is **2a** and this form makes a greater contribution to the resonance hybrid in the deuterated compound. The negative isotope effect results from a shift of the positive charge toward C3. The observation of a large positive value of $^3\Delta C(D) = +1.5$ ppm for carbon 3 is in agreement with this conclusion. The isotope effects suggest that a three-membered cyclic structure such as **2** is not appropriate for the mercurinium ion. If only the two π-electrons of the alkene and none of the electrons of Hg^{2+} (d^{10} configuration) are used in bonding then the mercurinium ion would have a bridging two-electron three-center bond as represented by **10**.

Acknowledgment. We are grateful to Dr. S. Prakash for advice on the preparation and for helpful discussion.

Registry No. 1 unlabeled, 25681-73-6; **2** unlabeled, 98778-45-1; **3** unlabeled, 563-79-1; **4** unlabeled, 594-81-0; **5** unlabeled, 594-60-5; **6** unlabeled, 5076-20-0; deuterium, 7782-39-0.

(8) The 2,3-dimethyl-2,3-butanediylbromonium ion was prepared by ionization of 2,3-dibromo-2,3-dimethylbutane by the previously reported procedure.[9] The ^{13}C chemial shifts are in satisfactory agreement with those previously reported[9]: $^{13}C\{H\}$ NMR (67.9 MHz, $CDCl_3$, 240 K) δ 26.6 (Cl, C4), 140.0 (C2, C3).

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(10) The 2,3-dimethyl-2,3-butanediylmercurinium ion was prepared by mercuration of 2,3-dimethyl-2-butene by the procedure of Olah et al.[11] The ^{13}C chemial shifts of the ion were similar to those reported of related derivatives.[11b]

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(12) In 2-(trideuteriomethyl)-3-methyl-2-butene-*1,1,1-d*$_3$ (**3**) and its derivatives, C2 has a longer relaxation time and lower intensity then C3.

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Selenium-77 Nuclear Magnetic Resonance Investigation of a Protein–Selenoligand Complex: Interaction of α-Chymotrypsin with (Phenylselenyl)acetate

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Of current interest in our laboratory is the development of selenium-77 NMR spectroscopy[2-7] and its application to biochemical investigations.[8] We have previously demonstrated the feasibility of observing selenium-77 resonances for selenium covalently attached to proteins.[8] We now demonstrate the first application of selenium-77 NMR spectroscopy to a protein–selenoligand complex, namely, a selenium-77 NMR investigation of the binding of a selenium-containing substrate analogue, (phenylselenyl)acetate, $PhSeCH_2COO^-Na^+$, to the enzyme α-chymotrypsin. (Phenylselenyl)acetate is the second product in the α-chymotrypsin-catalyzed hydrolysis of the substrate *p*-(nitrophenyl)(phenylselenyl) acetate and acts as an inhibitor for α-chymotrypsin.[9] The use of selenium-77 NMR for the investigation of biochemical systems is attractive for two reasons: (1) selenium can mimic oxygen, sulfur, and methylene functionalities in biomolecules[10] and (2) selenium-77 has a wide chemical shift range (2800 ppm).[11] This investigation was designed to address the question: Is selenium-77 chemical shift sensitivity sufficient to reflect the mechanism of binding of a selenium-containing inhibitor to α-chymotrypsin?

(1) Taken in part from the thesis of G. P. Mullen, to be submitted to the Department of Chemistry in partial fulfillment of the requirements of the Ph.D. degree.

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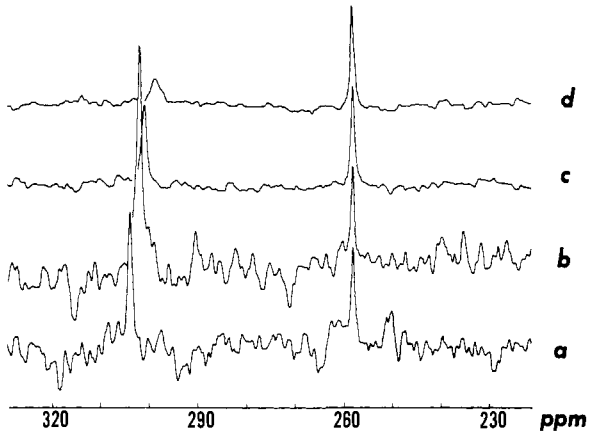

Figure 1. ^{77}Se NMR, 38.168 MHz, spectra obtained on a Bruker WP-200 with a 15-mm broad-band probe with proton gated decoupling (6-s delay), 45° pulse width, 16K data points zero filled to 32K, resolution 0.47 Hz/pt. Chemical shifts are internally referenced to $(CH_3)_3Se^+I^-$ (30 mM). Active α-chymotrypsin concentrations by cinnamoyl imidazole titration[12] and (phenylselenyl)acetate concentrations respectively are as follows: (a) 0, 46.0 mM, (b) 4.49, 75.4 mM, (c) 4.49, 30.2 mM, (d) 4.49, 11.9 mM, in 0.1 M K_2HPO_4 buffer, 10% D_2O, pH 6.82 ± 0.05 (uncorrected) and at a probe temperature of 295 ± 1 K. An exponential multiplication producing a line broadening of 30 Hz was applied to each FID before Fourier transformation.

It is noteworthy that this experiment was conducted with naturally abundant selenium-77 (7.58%), and spectra (Figure 1) were acquired in reasonable periods of time, i.e., 1.5 and 24 h for 75.4 and 11.9 mM (phenylselenyl)acetate, respectively. The spectra shown in Figure 1, which were obtained at 38.168 MHz, exhibit broadening of the (phenylselenyl)acetate resonance in the presence of 4.49 mM α-chymotrypsin with line widths of 22 ± 5 Hz for inhibitor concentrations of 13.6–75.4 mM as compared to 12 Hz in the absence of the enzyme. On lowering the inhibitor concentration to within 2.6 times that of the enzyme concentration, the line width of the (phenylselenyl)acetate resonance further broadened to 54 ± 5 Hz. The resonance of the internal standard, $(CH_3)_3Se^+I^-$ (30 mM), exhibited a line width of 4.0 ± 3.0 Hz, which was unaffected by the presence of the enzyme (4.49 mM) and/or the inhibitor. From Figure 1, it is apparent that $[E_0]/[I_0]$ ratios produce shifting of the resonance of (phenylselenyl)acetate. These data suggest a reversible enzyme–inhibitor complex with the inhibitor undergoing rapid exchange beween the enzyme bound and free states. This exchange was further characterized at 76.311 MHz under the same conditions as those stated in Figure 1. When inhibitor concentrations of 15.0 and 30.1 mM are used, the line widths were 152 ± 20 and 95 ± 20 Hz, respectively. The broadening observed at 76.311 MHz is consistent with a considerable exchange contribution to the transverse relaxation rates at this frequency.[13] The observed reduction of this broadening at 38.168 MHz is in agreement with the assignment of rapid exchange at this frequency. On the basis of an appropriate model for the enzyme–inhibitor interaction, the values of Δ and K_1 can be determined, where Δ represents the chemical shift difference between the free and enzyme-bound states of the ligand. We have determined these parameters on the basis of a two-site exchange enzyme–inhibitor equilibrium using eq 1 and 2, which are extensions of those originally presented by Raftery et al.[14] An accurate determination of K_1 and Δ can be made if the following requirements are met; (1) equal binding of the inhibitor to both monomeric and oligomeric[15–17] forms of α-chymotrypsin occurs, (2) no additional perturbation to the chemical shift, Δ, occurs for equal binding to monomeric and oligomeric forms of the enzyme, (3) no solvation-type shift occurs due to the volume percent of the enzyme in solution, and (4) the rapid exchange condition is completely fulfilled.[13,18] The plot of $-[E_0]/\delta[I_0]$ vs. $1/[I]$ for the iteratively determined K_1 (19.7 mM) is shown in Figure 2.[19] The Δ obtained from this analysis is −39.8 ppm (−1519 Hz), i.e., to higher shielding. This K_1 is comparable to the kinetically determined K_1 of 3-phenylpropanoate (25 ± 5 mM).[20] On the basis of the results of this study a lower limit of 6.7×10^3 s^{-1} is assigned to k_{off} for the (phenylselenyl)acetate–α-chymotrypsin complex.[21] This is of the same order of magnitude as the k_{off} obtained for the α-chymotrypsin–*N*-(trifluoroacetyl)-D-tryptophan complex.[22]

$$[E_0]\delta[I_0] = K_1/\Delta[I] + 1/\Delta \quad (1)$$

$$[I] = [I_0] - \{K_1 + [E_0] + [I_0] - [(K_1 + [E_0] + [I_0])^2 - 4[E_0][I_0]]^{1/2}\}/2 \quad (2)$$

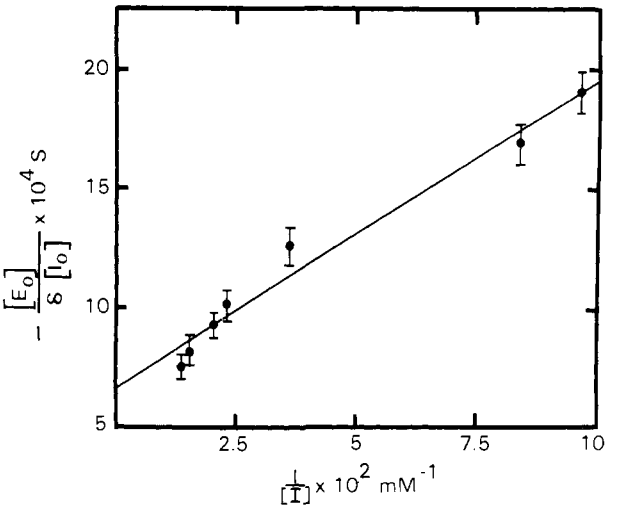

Figure 2. Plot of $-[E_0]/\delta[I_0]$ vs. $1/[I]$ from calculated values of [I] from eq 2 and iteratively matching the K_1 with the K_1 obtained in eq 1.

It appears that the requirements for an accurate determination of K_1 and Δ are satisfied by our data. For the plot in Figure 2 the curvature of a line connecting the data points at the lowest [I] is *not* in accordance with a decrease in [EI] due to enzyme oligomerization, since this would result in a *larger* value of $[E_0]/\delta[I_0]$. The fitting of this model is in agreement with reports of equal binding of the inhibitors 3-phenylpropanoate and 4-fluorocinnamate to monomeric, dimeric, and trimeric forms of α-chymotrypsin in a sedimentation[23] and fluorine-19 NMR study,[24] respectively. The assumption of rapid exchange can also be a source of considerable error in the analysis of K_1 and Δ.[13] However, we have shown that the exchange is rapid (i.e., $k_{off} > 13.4 \times 10^3$ s^{-1}) at 76.311 MHz and that K_1 is large; therefore, using criteria established by Feeney et al.,[13] we estimate *maximal* uncertainties of 19.7 ± 10 mM in K_1 and −39.8 ± 10 ppm in Δ.

The 39.8 ppm shift for the α-chymotrypsin–(phenylselenyl)-acetate complex is an order of magnitude larger than the Δ's

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previously determined for inhibitors containing the proton,[25,26] carbon-13,[27] and fluorine-19[24,28–31] probe nuclei. The −39.8 ppm shift observed for this exchange can arise from a combination of polar field[2] or polarizability[11,32] effects, conformational restrictions imposed by the active-site producing possible differences in the γ-effect,[4,11] and a chemically different intermediate(s) upon binding of (phenylselenyl)acetate to the enzyme. Clearly, the results of this investigation establish the capabilities of this multinuclear technique and provide precedent for similar selenium-77 NMR applications.

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Supplementary Material Available: A Table of observed chemical shifts, line widths, and predicted chemical shifts as a function of inhibitor concentration (1 page). Ordering information is given on any current masthead page.

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Measurement of Hydrazine, Hydrazine Radical Cation Self-Exchange Electron-Transfer Rates by ^{1}H NMR

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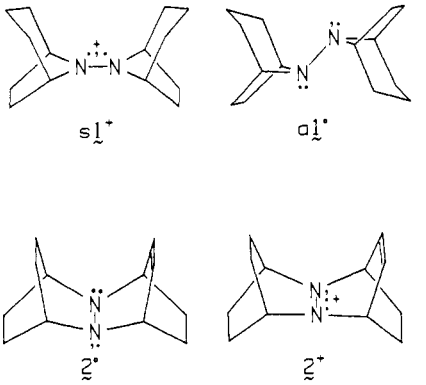
Electron loss from a hydrazine is accompanied by a large geometry change at the nitrogens, making hydrazine self-exchange electron-transfer reactions much slower than those for most other organic systems.[1] Although we have known for years that homogeneous electron transfer between hydrazines and hydrazine radical cations is unusually slow,[2] measurement of the rate constant, k_{et} in eq 1, has proven difficult. We recently exploited the

$$R_4N_2^+ + \underline{R_4N_2}^0 \overset{k_{et}}{\rightleftharpoons} R_4N_2^0 + \underline{R_4N_2}^+ \qquad (1)$$

unusual conformational properties of 8,8′-bi-8-azobicyclo-[3.2.1]octane[3] to give the first determination of a k_{et} value[3b] for a hydrazine. Electron transfer between the syn cation $\mathbf{s1}^+$ and the anti neutral isomer $\mathbf{a1}^0$ is exothermic by about 1.6 kcal, and k_{et} was estimated at 4.5×10^3 M^{-1} s^{-1} (22 °C, CH_3CN with 0.15 M n-Bu_4NClO_4) by simulation of cyclic voltammograms for oxidation of **1**. In the present work we report the first measurement of hydrazine, hydrazine radical cation self-exchange electron-transfer rates and provide a brief study of solvent and counterion effects.



2,7-Diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene (**2**) is prepared by the recently discovered proton-driven Diels–Alder reaction of 1,3-cyclohexadiene with protonated 2,3-diazabicyclo[2.2.2]oct-2-ene[4] and proves to be especially well suited for electron-transfer rate studies. Silver(I) oxidation of hydrazine **2** affords isolably stable radical cation salts $\mathbf{2}^+X^-$ (X = NO_3, PF_6, OTs). The electron pairs of **2** are held at the electronically most destabilizing 0° dihedral angle, and only one $\mathbf{2}^0$ and one $\mathbf{2}^+$ conformation are observed by magnetic resonance, making the electron-transfer process far simpler than in the case of **1**. The **2**, $\mathbf{2}^+$ electron transfer is rapid enough to cause substantial broadening of the ^{1}H NMR spectrum of $\mathbf{2}^0$ in the presence of $\mathbf{2}^+$; such broadening is not observed for **1**, $\mathbf{1}^+$ mixtures or their analogues.[1a] The vinyl hydrogen of $\mathbf{2}^0$ provides a convenient signal for quantitative determination of the amount of broadening because it is well separated from the other signals and is a sharp AA′BB′ multiplet, allowing accurate determination of the amount of exchange broadening, $\Delta\nu_{1/2} = (\nu_{1/2})_{2,2^+} - (\nu_{1/2})_2$, by simulation. Values of k_{et} are determined according to the slow exchange eq 2, introduced

$$k_{et} = \pi\Delta\nu_{1/2}/[\mathbf{2}^+] \qquad (2)$$

by McConnell and by Weissman almost 30 years ago.[5] Decomposition of hydrazine radical cations by neutral hydrazines can be a problem even for Bredt's Rule protected compounds, but ^{1}H NMR studies prove that $\mathbf{2}^+$ is not decomposed by **2** on the time scale of the kinetic experiments (ca. 30 min). Plots of broadening vs. $[\mathbf{2}^+]$ fit eq 2 very precisely; all r values determined in this work for such a plot are above 0.999. All peaks qualitatively broaden to the same extent, and no chemical shift dependence upon radical cation concentration was observed, as required for slow exchange. Table I summarizes k_{et} in six solvents near room temperature. The rate constants are reproducible to 5% and the $\Delta G_{et}^{\ddagger}$ values to 0.3%.

The largest effect seen in our data is a decrease in k_{et} in methanol by a factor of 13 compared to non-hydroxylic solvents of similar dielectric constant, ϵ. Hydrogen bonding to the neutral form is clearly implicated for this lowering of k_{et}. The k_{et} values observed do not follow the Marcus dielectric parameter[6] $(1/n^2 - 1/\epsilon)$ at all. Except for $CDCl_3$ and CD_3OD, there is a modest increase in k_{et} with decreasing ϵ, but the effect is an order of magnitude smaller than predicted by Marcus theory at reasonable distances for electron transfer. We note that $CDCl_3$ gives the smallest k_{et} for non-hydroxylic solvents despite having the lowest dielectric constant. Increased ion pairing effects relative to solvents of higher dielectric constant or the relatively weak hydrogen bonding of chloroform might be responsible. A modest decrease in k_{et} is observed as tetra-n-butylammonium perchlorate is added

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