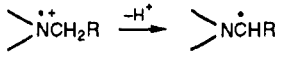
Table II. Relative Kinetic Acidity for



R	this work CH_3Cn	this work CH_3OH	lewis' work[1] CH_3CN	$E_{1/2}(+)$[1] Me_2NCH_2R (MeCN) (V vs SCE)	BDE H-CH_2R (kcal/mol)	calcd rel[d] pK_a values
H	0.01[b]	0.01[b]	1.1	0.76	104[14]	+16
CH_3	0.02[b]	0.02[b]	0.5	-	98[14]	-
$Si(CH_3)_3$	0.1[a,b]	-	-	-	99[15] (97)[16]	-
CO_2CH_3	0.5[c]	0.6[c]	2.3	0.96	91[17]	+3
Ph	1.0[c]	1.0[c]	1.0	0.90	85[14] (88)[18]	+1
$CH{=}CH_2$	1.9[c]	3.0[c]	0.5	0.92	85[14]	-1
$C{\equiv}CH$	3.9[c]	2.0[c]	ca. 111	1.23	89[19]	-3

[a] A lower limit based upon product detectability. [b] Comparisons are possible between H and CH_3, but only upper limits are possible in comparisons with others. [c] Comparisons are possible between CO_2CH_3, Ph, $CH{=}CH_2$, and $C{\equiv}CH$, but only lower limits are possible in comparisons with others. [d] Calculated by using the equation in ref 13a following conversion of $E_{1/2}(+)$ vs SCE to vs NHE (add 0.24 V) and using model hydrocarbon RCH_2-H BDE values. The calculated pK_a values are listed relative to R = Ph and should not be considered as absolute.

radical pair while the opposite effect is observed in the amino enone system. Also, the kinetic acidities at benzylic and methyl centers are the same in the former process whereas the current studies suggest that the Ph group more greatly enhances amine cation radical acidities.

The exact source or sources of these differences are not obvious.[12] Lewis has proposed that the alkyl substituent effects have a steric/stereoelectronic origin, i.e., deprotonation occurs along a line parallel with the half-vacant p_N orbital and more rapidly at the less substituted α-carbon. Steric factors alone might also be important in governing orientation of and, thus, deprotonation rates between partners in the stilbene-amine ion radical pair. However, why these factors would be less important in the amino enone system is not clear. Electronics should also play a major role in controlling amine cation radical acidities. The treatment of Arnold[13] suggests that the pK_a values of these intermediates should be governed by the amine oxidation potentials and the α-CH bond dissociation energies (see Table II). Indeed, the relative kinetic acidities of amine cation radicals determined by analysis of our results closely parallel the relative pK_a values, estimated by using Arnold's method (Table II). These studies have provided a new view of how substituents can affect the rates of deprotonation of amine cation radical intermediates.

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-8917725 and INT-8717920).

(12) (a) A referee has suggested that the differences might relate to the degrees of C-H bond breaking in the deprotonation transition states. Thus, the extent to which radical stabilizing substituents control kinetic acidities in these processes would be increased when the transition states for deprotonation occur later. It is noteworthy that the d-isotope effects found for the enone-amine reactions (ca. 5-6) in MeCN are much larger than those observed[1] (ca. 1.5) for the stilbene-amine system in MeCN. This perhaps reflects later C-H bond cleavage transition states in the former processes. However, it should be noted that small d-isotope effects (ca. 2.3) are associated with the amine-enone reactions in MeOH, yet the deprotonation selectivities are nearly the same as for the reactions occurring in MeCN. (b) Other results which may or may not relate to relative acidities of amine cation radicals are found in electrochemical studies; cf.: Smith, P. J.; Mann, C. K. *J. Org. Chem.* **1969**, *34*, 1821. Lindsay-Smith, J. R.; Masheder, P. *J. Chem. Soc., Perkin Trans. 2* **1976**, 47. Palasz, P.; Utley, J. H. P.; Hardstone, J. D. *J. Chem. Soc., Perkin Trans. 2* **1984**, 807. Shono, T.; Toda, T.; Oshino, N. *J. Am. Chem. Soc.* **1982**, *104*, 2639. Shono, T.; Hamaguchi, H.; Matsumura, Y. *J. Am. Chem. Soc.* **1975**, *97*, 4264. Fuchigami, T.; Nakagawa, Y.; Nonaka, T. *J. Org. Chem.* **1987**, *52*, 5489.

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$$pK_a = \frac{BDE - 37.6}{1.36} - \frac{E_{1/2}(+)}{0.0592}$$

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Site-Specific Bond Cleavage Leading to Hydrogen Atom Production in the Photolysis of 2-Iodopropane

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Selective bond cleavage continues to be a topic of considerable interest in photochemical studies on small molecules.[1,2] Recently, attempts to understand and influence photolysis reactions that involve competing H and D atom channels in HOD[3-5] and HC_2D[6] have produced notable results. These interesting experiments focus on understanding and/or controlling the H versus D competition that occurs with respect to bond cleavage at a particular reactive site. In related but somewhat different experiments, we demonstrate how H and D atoms can be used as labels to investigate photolysis involving competition *between* chemically distinct reactive sites. The question is not whether H or D is formed. Rather, H and D are used as labels to determine at which site bond cleavage occurs.

When 2-iodopropane is photolyzed with 193- or 248-nm excimer laser radiation under collisionless conditions, we observe substantial H atom production. Presumably, the C-I bond is broken initially; thus the remaining radical has chemically distinct carbon atoms that can be labeled initially by using selectively deuterated 2-iodopropane. As a result, "site-specific" atomic hydrogen gen-

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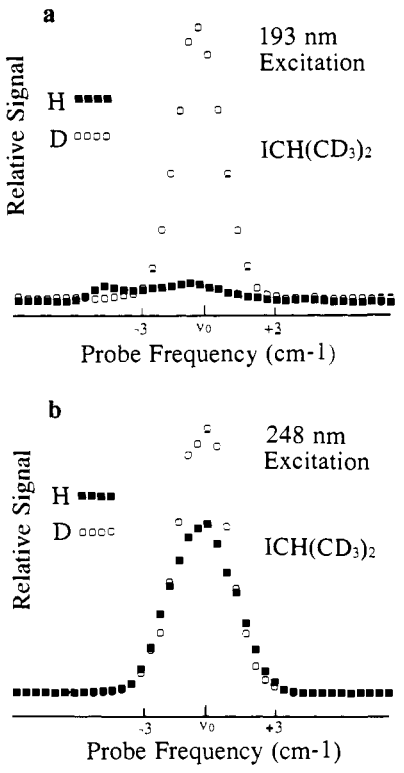

Figure 1. H atom and D atom Doppler profiles resulting from the photolysis of $ICH(CD_3)_2$ at (a) 193 nm and (b) 248 nm. Clearly, C–H bond cleavage is enhanced at 248 nm. For the H atom signal, ν_0 = 82259.1 cm^{-1}. For the D atom signal, ν_0 is shifted upward in energy from this value by 22 cm^{-1}.

eration can be studied, with the results providing information about dissociation processes in the isopropyl radical intermediate. Our previous investigation on iodoethane showed that C–H bond cleavage caused by 193-nm excimer laser photolysis was observed to be probabilistic; that is, the data showed no preference for C–H bond dissociation from the α or β carbon atom.[7] However, photolysis at 248 nm displayed a *clear* preference for C–H bond dissociation from the β carbon site.[7] In this communication, results on selectively deuterated 2-iodopropanes (compounds I and II) are reported. For example, the 193-nm photolysis of compound

I produces a D:H ratio of 7:1, not particularly surprising given the initial ratio of 6:1 found in the parent molecule. Relative to the 193-nm data, however, 248-nm photolysis clearly enhances H atom production from the α carbon site to the point where the D:H ratio is near unity.

The experimental arrangement is described in detail elsewhere.[8,9] Briefly, 2-iodopropane (Aldrich; 99%), 2-iodopropane-*1,1,1,3,3,3-d*$_6$ (MSD; 98% enriched), or 2-iodopropane-*2-d* (MSD; 99.6% enriched) is introduced without further purification into the ionization region of a time-of-flight mass spectrometer. Each sample pressure was maintained at 2×10^{-4} Torr above a background pressure of 2×10^{-6} Torr, and photolysis was achieved by using an excimer laser (Questek 2220). The probe pulse from an excimer pumped dye laser (Lambda Physik LPX 105; FL3002) follows after a 40-ns delay, and this output pulse (~365 nm) is frequency tripled in Kr gas and scanned through the Lyman α transition (121.6 nm) to obtain a Doppler profile. H atoms are detected via two-photon ionization (121.6 ± 364.7 nm),[10] and D atoms are detected in the same manner except that the initial transition is 22 cm^{-1} higher in frequency.

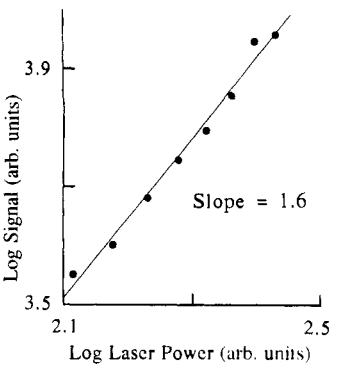

Figure 2. A log–log plot displaying experimental data on H atom production as a function of 248-nm photolysis laser power.

Results for the 193-nm photolysis of the hexadeutero compound I are presented in Figure 1a. Shown are Doppler profiles of H and D atoms taken under identical conditions except for the probe laser frequency. (Note that the cross sections for the Lyman α transitions in H and D are the same.)[5] The molecule itself has a D:H ratio of 6:1; which would be the expected ratio for totally random H or D atom formation. By comparing areas under the two curves, a statistical-type distribution of 7:1 is obtained for the D:H ratio. Whether or not the overall process is in fact statistical requires further experimentation. In Figure 1b, compound I has also been photolyzed, only this time using 248-nm light. Clearly, under these conditions the probability of C–H bond cleavage at the α carbon site has increased substantially. The raw profiles yield a D:H ratio of 1.2:1, an increase in H atom production of a factor of 6 at the α carbon site compared with the 193-nm data. Confirming experiments (not shown) were also conducted at 193 and 248 nm on compound II, the "isotopic inverse" of compound I. Similarly, enhancement was observed for bond cleavage at the α site when 248-nm radiation was used.

We suspect that the observed enhancement at the α carbon may result from a second photon absorption, most likely by the isopropyl radical. Figure 2 shows a typical log signal vs log power plot for H atom production from undeuterated 2-iodopropane at 248 nm: the slope is 1.6. At 248 nm, initial photon absorption by 2-iodopropane accesses the broad and structureless A band, where the final state of the molecule is thought to be directly dissociative.[11,12] At this wavelength (248 nm), the isopropyl radical possesses a reasonable absorption cross section of $\sim 10^{-18}$ cm^2.[13] Consequently, secondary photon absorption is quite possible, and the slope is indicative of the existence of a route to atomic hydrogen production that is at least two-photon. The fact that the slope of the power response plot is not closer to 2 may be the result of a competing one-photon route which also produces H atoms, or one of the electronic transitions involved may be saturating. These issues and the exact role of the second photon absorption remain to be addressed.

When compared with 193-nm data or a simple statistical prediction, we have demonstrated that excitation into the A band of 2-iodopropane at 248 nm produces C–H bond cleavage with a definite propensity toward the α carbon site. In addition to improving our understanding of "site-specific" bond cleavage in 2-iodopropane, we are investigating other halocarbon molecules as well. Understanding the origin of such effects could ultimately lead to photochemical enhancement and/or control of these important molecules.

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Torsional Effects in Glycoside Reactivity: Saccharide Couplings Mediated by Acetal Protecting Groups†,‡

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The use of protecting groups in synthetic carbohydrate chemistry is unavoidable, and since esters and ethers are chemically different, *O*-acyl and *O*-benzyl groups are favorites for "temporary" and "persistent" protection,[1] respectively. However, these groups profoundly affect the reactivity of glycosyl donors,[2] and under the armed/disarmed rubric,[3] we recently disclosed[4] that these reactivity differences provided a basis for chemoselective assembly of oligosaccharides.[5] Cyclic acetals[6] such as shown in Chart I are also temporary[1] protecting groups, and the fact that 1,3-dioxane or 1,3-dioxolane derivatives can be formed competitively[7,8] has made their use a mainstay of synthetic carbohydrate chemistry.[9] However, in this manuscript we disclose that cyclic acetals profoundly affect pyranoside reactivity, thereby paving the way for an armed/disarmed protocol based on torsional effects, complementary to that disclosed earlier[4] which was based on electronic effects.[10]

The ability to "oxidatively hydrolyze" *n*-pentenyl glycosides (NPGs) under neutral conditions allows us to cleave the anomeric center without affecting other acid-sensitive functionalities,[11,12] and in the course of exploiting this potential,[12] we were struck by the range of relative reaction rates of compounds **1b–4b** (Table I, entry a). These results suggested that it might be possible to use cyclic acetals not only for the traditional protecting group role but also to induce chemoselectivity in the formation of cyclic oxo carbenium ions.

Our first requirement was to carry out a sophisticated conformational analysis as a basis for predicting reactivity. While the ground-state conformations of the starting pyranosides were expected to be $^4C_1$ chairs, those for the oxo carbenium ions had to be determined. PM3[13] was chosen for this task, because of its capability to analyze both ground states and reactive intermediates. The C_5O_5–C_1C_2 dihedral angle (ω) is ideally 0° in oxo carbenium ions, and hence the conformational energies of the ions derived from the tetra-*O*-methyl glycosides **1a**, **5a**, and **7a** were determined. The energy curves for the oxo carbenium ions derived from **1a**, **5a**, and **7a**, as determined by PM3, are parabolic with minima at 0°, which confirms planarity of the $C_5O_5^+$–C_1C_2 segments with perfect π overlap. For the conformationally restrained glucosides **3a** and **4a**, the energy curves are still parabolic but the minima have been shifted to +20°.

With PM3 data therefore available for both glycosides and oxo carbenium ions, the relative activation energies (E_a) could now be computed,[14] and these are shown in Table I. Their validity could be checked against known experimental rates of hydrolysis. Thus the computed activation energies for **1a**, **3a**, and **4a** are in keeping with the experimental rates for oxidative hydrolysis[11,12] of **1b**, **3b**, and **4b**, respectively (Table I, entries a and b). Similarly the reactivity trends galacto > manno > gluco of Isbell and Frush[15] were upheld in our studies (Table I, entries c and d).

The computed values in Table I therefore implied that acetalated species such as **2**, **6**, and **8** should react less readily than their torsion-free analogues **1**, **5**, and **7**, respectively. These predictions were borne out by the rates for the oxidative hydrolysis of **1b**/**2b**, **5b**/**6b**, and **7b**/**8b** (Table I, entry c). The corresponding computed values (Table I, entry d) show how well the $\Delta\Delta E_a$ values predict these reactivity trends.

These developments suggest a strategy for disarming glycosyl donors based solely on the presence of acetal protecting groups. Indeed it proved possible to chemospecifically couple glucosides **1b** + **2c**,[16] mannosides **5b** + **6c**, and galactosides **7b** + **8c** to give **9**, **10**, and **11**, respectively,[17] with no evidence for self-condensation

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(17) Experimental procedure: In a typical experiment the acetalated alcohol donor (e.g., **6c**, 1.5 mM), the glycosyl donor (e.g., **5b**, 1.0 mM), and iodonium dicollidine perchlorate[18] (2.0 mM) were dissolved in THF (10 mL). The reaction was followed by TLC (petroleum ether/ethyl acetate mixtures, 3:1) until the alcohol disappeared or until there was no further change. The R_f of the disaccharide usually fell between the two reactants. The coupling was complete in 1–2 h. The reaction mixture was diluted with anhydrous ether and filtered and the filtrate washed with 10% aqueous sodium thiosulfate solution and brine. The organic extract was dried over Na_2SO_4, filtered, and concentrated in vacuo. Flash chromatography afforded the cross-coupled disaccharides **9**, **10**, and **11** in 52%, 41%, and 54% unoptimized yields. Identification of the cross-coupled products was facilitated by the fact that both reactants had different protecting groups. On this basis, we have failed to detect products resulting from self-coupling of the acetalated alcohols.

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