center with three meridionally situated PMe_3 ligands, a phenyl ligand, and what can best be described as a substituted σ-butadienyl ligand. While there appears to be no group in the sixth coordination site, one of the methyl groups from a *tert*-butyl fragment on the butadienyl chain sits over that sixth site at a distance of 2.782 Å, suggesting that there is an agostic Ir–H–C interaction occurring at that site.[8] While hydrogen atoms were not located in this structure, further support for an agostic interaction was obtained from low-temperature ^{1}H NMR.[9]

We propose that **2** is formed by the sequence of reactions shown in Scheme I. Following chloride removal to generate a coordinatively unsaturated iridium center, the *tert*-butylacetylene "inserts" into the Ir–H bond to form an iridium–vinyl intermediate. A second equivalent of *tert*-butylacetylene adds to this still coordinatively unsaturated complex.[10] The second *tert*-butylacetylene then rearranges to a *tert*-butylvinylidene group.[11] The final product is formed by migration of the vinyl group to the α-carbon of the vinylidene moiety with the agostic interaction between the iridium and one of the *tert*-butyl methyl hydrogens stabilizing the final product. Several deuterium labeling experiments fully support this mechanism. If **1** with hydride replaced by deuteride is allowed to react with 2 equiv of ^{t}BuC≡CH, the deuterium is found exclusively at postion 4 (refer to the numbering used for **2** in Scheme I). Reaction between hydrido **1** and 2 equiv of ^{t}BuC≡CD gave complementary results, i.e., D located at positions 1 and 3. When hydride **1** is allowed to react sequentially with 1 equiv of ^{t}BuC≡CH followed by 1 equivalent of ^{t}BuC≡CD after a short time delay, the deuterium is predominantly incorporated at position 1.

The mechanism shown in Scheme I suggests that this iridium system may allow for further additions leading to the oligomerization of alkynes. Following the vinyl to vinylidene migration, the complex is still formally a coordinatively unsaturated metal vinyl complex in the absence of the stabilizing agostic interaction. A third equivalent of alkyne could then add and rearrange to a vinylidene, and the sequence could continue building up oligomers of alkynes with a branched structure. Preliminary information suggests that this may indeed be possible.[12]

In this work we have demonstrated an unusual reaction involving the coupling of two alkynes on iridiun via a vinyl to vinylidene migration pathway. The iridium complex isolated from the reaction of *tert*-butylacetylene is an unusual butadienyl compound stabilized by a δ-agostic interaction. We believe this work lays the foundation for future investigations into developing the vinyl to vinylidene migration into a synthetically useful reaction with an eye toward the synthesis and characterization of novel branched acetylene oligomers and polymers.

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Supplementary Material Available: Tables 1–5 including a structure determination summary, atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for **2** (5 pages). Ordering information is given on any current masthead page.

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[7] X-ray data for **2**: orthorhombic space group *Pbac*, $a = 11.658$ (4) Å, $b = 18.041$ (4) Å, $c = 33.731$ (8) Å with $Z = 8$. A total of 7449 independent reflections were collected (3.5–55° in 2θ) with 4878 observed ($F > 3.0\sigma(F)$); 344 variables refined to yield $R = 6.2\%$ and $R_w = 6.28\%$ with goodness-of-fit = 1.77. Full details are available in the supplementary material.

[8] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[9] On cooling, the broad *tert*-butyl singlet found at δ 0.53 in the ^{1}H NMR spectrum broadens further and collapses into the base line at −20 °C. On further cooling (−90 °C is the lowest we measured), two new resonances grow at δ −0.7 and 1.1 ppm. This indicates that we are freezing out the process that averages the three *tert*-butyl methyl groups, but rotation of the methyl coordinated to the iridium is still a fast process at −90 °C.

[10] Examples of iridium with both vinyl and η^2-alkyne ligands have been observed: (a) Baddley, W. H.; Fraser, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3661. (b) McClure, G. L.; Baddley, W. H. *J. Organomet. Chem.* **1971**, *27*, 155. (c) Baddley, W. H.; Tupper, G. B. *J. Organomet. Chem.* **1974**, *67*, C16.

[11] The rearrangement of a coordinated alkyne to a vinylidene is a well-documented process: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59 and references therein.

[12] Treatment of **1** with Tl[PF$_6$] in the presence of acetylene leads to a rapid reaction to produce a dark, purple oily material which has yet to be fully characterized but appears to be a branched acetylene oligomer.

Deuterium Isotope Effects in Gas-Phase Reactions of Alkyl Halides: Distinguishing E2 and S_N2 Pathways

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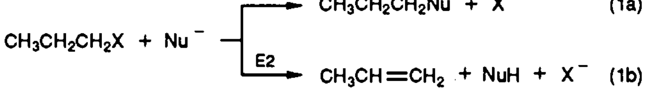
While E2 and S_N2 reactions of alkyl halides are among the most studied of all chemical processes in solution, investigations of their gas-phase ion–molecule counterparts have been greatly hindered by the difficulty of distinguishing between the two pathways.[1] This is the case because in most gas-phase experiments only the ions are detected, and halide is the exclusive ionic product of both reactions (eq 1).



$$CH_3CH_2CH_2X + Nu^- \xrightarrow{S_N2} CH_3CH_2CH_2Nu + X^- \qquad (1a)$$

$$CH_3CH_2CH_2X + Nu^- \xrightarrow{E2} CH_3CH{=}CH_2 + NuH + X^- \qquad (1b)$$

We report that with the proper choice of nucleophiles S_N2 and E2 reactions of halides can be distinguished in the gas phase, as in solution, by their differing deuterium kinetic isotope effects,[2] the former showing an inverse secondary k_H/k_D as small as 0.76 and the latter a normal primary k_H/k_D as large as 4.7.

What little information is available in the literature about this competition is conflicting. By using very difficult neutral detection techniques two groups of workers have come to rather different conclusions in what seem to be similar systems. Lieder and Brauman[3] observed substitution products in the reaction of fluoride ion with ethyl chloride in an ion cyclotron resonance spectrometer, whereas Jones and Ellison[4] detected only the elimination product, propylene, in the reaction of methoxide ion with *n*-propyl bromide in a flowing afterglow apparatus. When the leaving group is not a halide ion, the different paths can sometimes be distinguished by the formation of different product ions. For example, ethers,[5] formates,[6] nitrites,[7] and cyclic sulfides[8] have been shown to undergo elimination rather than substitution, even when the leaving group is primary, while sulfites[9] lead to nearly equal amounts of substitution and elimination.

Only a few kinetic isotope effects have heretofore been detected in gas-phase ion–molecule chemistry,[5c,10] primarily because these reactions are so rapid, with measurable rate constants in the range 10^{-9}–10^{-13} cm^3 molecule^{-1} s^{-1} (10^8–10^{12} L mol^{-1} s^{-1}). Most alkyl halides react with nucleophiles at or near the collision rate, making

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[1] Riveros, J. M.; Jose, S. M.; Takashima, I. *Adv. Phys. Org. Chem.* **1985**, *21*, 197.

[2] Melander, L.; Saunders, J. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley and Sons: New York, 1980.

[3] Lieder, C. A.; Brauman, J. I. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *16*, 307.

[4] Jones, M. E.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 1645.

[5] (a) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034. (b) DePuy, C. H.; Beedle, E. C.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1982**, *104*, 6483. (c) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715.

[6] Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049.

[7] (a) King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133. (b) Noest, A. J.; Nibbering, N. M. M. *Adv. Mass Spectrom.* **1980**, *8*, 227.

[8] Bartmess, J. E.; Hays, R. L.; Khatri, H. N.; Misra, R. N.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4746.

[9] Lum, R. C.; Grabowski, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 8568.

[10] Bierbaum, V. M.; Filley, J.; DePuy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2818.

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Table I. Rate Coefficients[a] and Isotope Effects for Reactions of Alkyl Halides with Nucleophiles

reagent:	$CF_3CH_2O^-$	H_2NS^-	$CF_3CF_2CH_2O^-$	HS^-	$(CF_3)_2CHO^-$	Cl^-	Br^-
PA[b] (kcal mol^{-1})	362	362	357	351	345	333	323
chlorides							
MeCl	2.20 ± 0.02 (−10)	1.46 ± 0.07 (−10)	1.01 ± 0.02 (−10)	1.21 ± 0.03 (−11)			
EtCl	2.48 ± 0.05 (−10)	3.81 ± 0.14 (−11)	5.88 ± 0.15 (−11)	nr[c]			
i-PrCl	4.31 ± 0.19 (−10)	nr	8.46 ± 0.36 (−11)	nr			
i-PrCl-d_6	1.88 ± 0.05 (−10)	nr	1.79 ± 0.09 (−11)	nr			
k_H/k_D	**2.3 ± 0.1**		**4.7 ± 0.3**				
t-BuCl	6.07 ± 0.35 (−10)	nr	1.69 ± 0.05 (−10)	nr			
t-BuCl-d_9	2.85 ± 0.09 (−10)	nr	5.14 ± 0.33 (−11)	nr			
k_H/k_D	**2.1 ± 0.1**		**3.3 ± 0.2**				
bromides							
MeBr	8.93 ± 0.20 (−10)	7.04 ± 0.03 (−10)	8.48 ± 0.21 (−10)	3.17 ± 0.10 (−10)	2.74 ± 0.13 (−11)	2.72 ± 0.14 (−11)	
MeBr-d_3		6.75 ± 0.18 (−10)	8.58 ± 0.18 (−10)	3.27 ± 0.03 (−10)	3.14 ± 0.01 (−11)	3.40 ± 0.19 (−11)	
k_H/k_D		**1.04 ± 0.03**	**0.99 ± 0.04**	**0.97 ± 0.03**	**0.87 ± 0.04**	**0.80 ± 0.06**	
EtBr	1.24 ± 0.04 (−9)	9.05 ± 0.16 (−10)	9.86 ± 0.42 (−10)	1.95 ± 0.13 (−10)	7.83 ± 0.33 (−12)		
EtBr-d_5	1.13 ± 0.04 (−9)	9.07 ± 0.29 (−10)	8.52 ± 0.29 (−10)	1.91 ± 0.05 (−10)	6.71 ± 0.35 (−12)		
k_H/k_D	**1.10 ± 0.06**	**1.00 ± 0.04**	**1.16 ± 0.06**	**1.02 ± 0.07**	**1.17 ± 0.08**		
i-PrBr	1.39 ± 0.04 (−9)	3.49 ± 0.09 (−10)	1.07 ± 0.02 (−9)	2.05 ± 0.05 (−12)	4.24 ± 0.17 (−12)		
i-PrBr-d_6	1.16 ± 0.03 (−9)	3.34 ± 0.03 (−10)	8.14 ± 0.41 (−10)	2.25 ± 0.11 (−12)	<2.20 (−12)		
k_H/k_D	**1.20 ± 0.05**	**1.04 ± 0.03**	**1.32 ± 0.07**	**0.91 ± 0.05**	**>1.9**		
t-BuBr	1.33 ± 0.01 (−9)	1.30 ± 0.05 (−10)	1.16 ± 0.08 (−9)	nr			
iodides							
MeI				7.44 ± 0.14 (−10)		1.66 ± 0.03 (−10)	2.89 ± 0.09 (−11)
MeI-d_3				7.35 ± 0.20 (−10)		1.98 ± 0.02 (−10)	3.78 ± 0.08 (−11)
k_H/k_D				**1.01 ± 0.03**		**0.84 ± 0.02**	**0.76 ± 0.03**

[a] Units are cm^3 molecule^{-1} s^{-1}. Errors are 1 standard deviation and reflect relative accuracy. Absolute errors, approximately ±20%. [b] Proton affinity of the nucleophile. [c] No reaction.

isotope effects undetectable. We have recently completed a comprehensive survey of the rates of reaction of primary, secondary, and tertiary chlorides and bromides with a variety of nucleophiles in the gas phase.[11] From this study we were able to identify nucleophiles that react relatively inefficiently, thereby giving isotope effects an opportunity to manifest themselves. We also came to the unexpected conclusion that, while sulfur and oxygen anions of the same basicity react at essentially the same rate by the S_N2 mechanism, oxygen anions are much more efficient than sulfur anions in inducing E2 reactions. For example, as shown in Table I, methyl chloride, which must undergo substitution, reacts somewhat more rapidly with H_2NS^- than with $CF_3CF_2CH_2O^-$. In contrast, isopropyl and *tert*-butyl chloride fail to react with H_2NS^- but react readily with the alkoxide. We therefore concluded that the latter reactions are eliminations.

These conclusions are confirmed by the isotope effects reported in this paper. As Table I shows, methyl bromide and iodide show either no isotope effect or an inverse secondary isotope effect with nucleophiles of all types. For example, CD_3Br reacts with Cl^- 1.25 times more rapidly than does CH_3Br. Thus the zero point energy difference between hydrogen and deuterium is greater in the transition state than it is in the ground state. These results are consistent with those reported for S_N2 reactions in solution.[12] In contrast, ethyl, isopropyl, and *tert*-butyl chlorides and bromides show appreciable to large isotope effects with appropriate nucleophiles whose attacking atom is oxygen, but no isotope effect with those nucleophiles with sulfur as the attacking atom. For example, isopropyl chloride reacts 4.7 times more rapidly with pentafluoropropoxide ion than does its hexadeuterio analogue, and *tert*-butyl chloride reacts 3.3 times more rapidly than does *tert*-butyl chloride-d_9. We have not found a sulfur nucleophile that reacts with either of these chlorides at a measurable rate. However, a comparison among sulfur and oxygen anions can be made using alkyl bromides as substrates. As predicted, sulfur anions react with ethyl and isopropyl bromide with no isotope effect or with a slight inverse isotope effect while oxygen anions react with these same substrates with appreciable normal isotope effects. The most reasonable explanation is that the former react by S_N2 and the latter mainly by E2 reactions.

The observation of such relatively large isotope effects in such rapid processes serves to emphasize yet again how the unique energetics of gas-phase ion–molecule interactions can give rise simultaneously to fast yet selective reactions. The ability to measure such subtle effects in the solvent-free environment of the gas phase should allow more precise computational modeling and perhaps give rise to a better understanding of the nature of isotope effects, particularly those secondary ones associated with the S_N2 reaction.[13]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation under Grants CHE-8815459 and CHE-8815446 and discussions with Prof. Saul Wolfe.

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(11) DePuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 8650.

(12) (a) Axelsson, B. S.; Matsson, O.; Langstrom, B. *J. Am. Chem. Soc.* **1990**, *112*, 6661. (b) Westaway, K. C. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1987; Vol. 7, p 275.

(13) For recent theoretical analyses of secondary isotope effects in S_N2 transition states, see: Zhao, X. G.; Tucker, S. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 826. Wolfe, S.; Kim, C.-K. *J. Am. Chem. Soc.*, submitted.

Photoinduced Porphyrin-to-Quinone Electron Transfer across Oligospirocyclic Spacers

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Structural determinations of bacterial photosynthetic reaction centers[2,3] have prompted many studies of photoinduced intramolecular electron transfer (ET) in models having linked porphyrins,[4,5] porphyrin–quinones (PQ)[5,6] and other donor–acceptor

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(1) (a) Rutgers University. (b) Washington University.

(2) Deisenhofer, J.; Michel, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 829–47.

(3) (a) Feher, G.; Allen, J. P.; Okamura, M. Y.; Rees, D. C. *Nature* **1989**, *339*, 111–6. (b) Norris, J. R.; Schiffer, M. *Chem. Eng. News* **1990**, *68*(31), 22–37.

(4) (a) Sessler, J. L.; Johnson, M. R.; Lin, T.-Y.; Creager, S. E. *J. Am. Chem. Soc.* **1988**, *110*, 3659–61. (b) Osuka, A.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Tamai, N. *J. Am. Chem. Soc.* **1990**, *112*, 4958–9. (c) Johnson, S. G.; Small, G. J.; Johnson, D. G.; Svec, W. A.; Wasielewski, M. R. *J. Phys. Chem.* **1989**, *93*, 5437–44.

0002-7863/91/1513-4010$02.50/0