Noble Gas–Actinide Compounds: Complexation of the CUO Molecule by Ar, Kr, and Xe Atoms in Noble Gas Matrices

Jun Li,[1,2] Bruce E. Bursten,[1]* Binyong Liang,[3] Lester Andrews[3]*

The CUO molecule, formed from the reaction of laser-ablated U atoms with CO in a noble gas, exhibits very different stretching frequencies in a solid argon matrix [804.3 and 852.5 wave numbers (cm^{-1})] than in a solid neon matrix (872.2 and 1047.3 cm^{-1}). Related experiments in a matrix consisting of 1% argon in neon suggest that the argon atoms are interacting directly with the CUO molecule. Relativistic density functional calculations predict that CUO can bind directly to one argon atom (U-Ar = 3.16 angstroms; binding energy = 3.2 kilocalories per mole), accompanied by a change in the ground state from a singlet to a triplet. Our experimental and theoretical results also suggest that multiple argon atoms can bind to a single CUO molecule.

Bartlett's synthesis of $XePtF_6$ in 1962 launched the rich chemistry of the noble gas (Ng) elements (*1*, *2*). Two recent developments have expanded the motifs for noble gas bonding (*3*, *4*). Räsänen *et al.* reported a stable neutral argon species, HArF, produced via the irradiation of HF in frozen Ar (*5*, *6*), and Seidler and Seppelt characterized the $[AuXe_4]^{2+}$ ion, in which the Xe atoms act as electron donors to the electron-deficient Au^{2+} ion (*7*, *8*). Here we report bonding between noble gas atoms and an actinide metal atom. These developments began with our observation that the CUO molecule, which we have trapped in noble gas matrices, exhibits notably different spectroscopic behavior in the presence of Ar, Kr, or Xe than in matrices of pure Ne. Experiments with mixtures of noble gases, coupled with theoretical calculations, provide strong evidence for direct bonds between Ar, Kr, or Xe atoms and the U atom of the CUO molecule.

The reaction of laser-ablated U atoms with CO during condensation in excess Ne at 4 K shows several interesting products, including the CO insertion product CUO. The vibrations of CUO were assigned through infrared (IR) spectroscopy coupled with the use of different isotopomers of CO. The $^{12}CU^{16}O$ molecule exhibits IR absorptions at 872.2 cm^{-1} (primarily due to the U-O stretch) and 1047.3 cm^{-1} (primarily due to the U-C stretch) in the Ne matrix (Fig. 1A), which is consistent with multiple C-U and U-O bonding (*9*). The neutral CUO molecule is isoelectronic with the well-known uranyl dication, UO_2^{2+}, which is linear and has a closed-shell $^1\Sigma^+$ ground state (*10*). Our calculations using relativistic density functional theory (DFT) predict an analogous linear geometry and closed-shell configuration for the isolated CUO molecule. The calculated frequencies, IR absorption intensities, and isotopic frequency ratios of the U-O and U-C stretching modes of the $^1\Sigma^+$ CUO molecule are in excellent agreement with the Ne matrix experimental values, which provides evidence that the molecule is linear and has a closed-shell electronic structure, and that there are no significant interactions between CUO and the Ne matrix (*9*).

When the same experiment is performed with an Ar matrix, the U-O and U-C stretching frequencies of $^{12}CU^{16}O$ are reduced to 804.3 and 852.5 cm^{-1}, respectively (Fig. 1C) (*11*, *12*). These large 67.9 and 194.8 cm^{-1} stretching frequency shifts cannot be attributed to simple matrix effects, which are typically 5 to 20 cm^{-1} (*13*). Such bands in the Ar matrix could be due to a low-lying first excited state ($^3\Phi$) of the CUO molecule, stabilized by the increased polarizability of the Ar matrix (*12*). For the isolated molecule, this excited state lies only about 1 kcal/mol above the ground state, a much smaller gap than the corresponding gap in UO_2^{2+} because of the higher lying atomic orbitals of the C atom relative to those of an O atom. Further, the C-U bond in the $^3\Phi$ state is weakened far more than the U-O bond relative to the $^1\Sigma^+$ state, which is consistent with the experimental observation. However, the calculated dipole moment of the singlet ground state of CUO (3.5 D) is greater than that for the triplet excited state (2.4 D), so we would expect any dipole–induced dipole interactions between CUO and the noble gas matrix to be greater for the ground state than for the excited state (*14*). Thus, such a polarizability-induced ground state reversal seems unlikely for a free CUO molecule.

We next performed supermolecular DFT calculations of the CUO molecule in axially symmetric Ng_{18} and Ng_{20} (Ng = Ne, Ar) cages. These symmetry-constrained calculations indicated that the Ar matrix as a nonbonding medium did not reverse the ground state of CUO from the $^1\Sigma^+$ singlet to the $^3\Phi$ triplet, as we originally proposed. However, when we allowed the system to relax the constraint of axial symmetry, the CUO molecule migrated to an Ar atom. We report below additional experimental and theoretical data that support the existence of the first noble gas actinide complexes, $CUO{\cdot}Ng_x$ (Ng = Ar, Kr, Xe; $x \geq 1$), that exhibit direct and significant interactions between the noble gas atoms and the U atom.

The large stretching frequency shifts for CUO when the matrix is changed from Ne to Ar are observed for matrices of Kr and of a Xe/Ar mixture as well (Table 1). When generated in Kr or Xe/Ar, the stretching frequencies of CUO are slightly red-shifted from those in Ar, indicating that the molecule is probably in the same electronic state in all three of these heavier noble gases. We used isotopomers of CO ($^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$) to identify the peaks of CUO and to determine the isotopic shifts of the U-O and U-C stretching modes of the molecule. In order to ascertain whether the red shifts are caused by the increased polarizability of the host matrix or by specific interactions between the CUO molecule and noble gas atoms, we also generated CUO in mixtures of noble gases. The results using a matrix of 1% Ar in Ne provide the most compelling evidence that a distinct complex is made between CUO and Ar atoms. The IR spectrum

Table 1. Infrared stretching frequencies (cm^{-1}) for CUO in various solid noble gas matrices for the predominant internal coordinate that changes in the stretching mode.

	Noble gas host					
Mode	Ne	Ar	Kr	1% Ar in Ne	1% Kr in Ar	1% Xe in Ar
U-O	872.2	804.3	797.1	806.5	803.1	801.3
U-C	1047.3	852.5	842.3	854.0	851.0	848.0

---

[1]Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA. [2]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA. [3]Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA.

*To whom correspondence should be addressed. E-mail: bursten.1@osu.edu (B.E.B.); lsa@unix.mail.virginia.edu (L.A.)

after photolysis and annealing of U + CO in a matrix of 1% Ar in Ne is shown in Fig. 1B. Although this Ne-dominant matrix has nearly the same polarizability as pure Ne, the peaks due to $^1\Sigma^+$ CUO (1074.2 and 872.2 cm^{-1}) are extremely weak in the Ar/Ne matrix relative to the Ne matrix. The dominant peaks due to CUO are two broad doublets (856.5 and 854.0 cm^{-1}; 808.0 and 806.5 cm^{-1}) that are very close in frequency to the bands observed at 852.5 and 804.3 cm^{-1} for CUO in a pure Ar matrix (Fig. 1C). Upon initial deposition at 4 K, the 856.5 cm^{-1} band is more intense than the 854.0 cm^{-1} band, but upon annealing, the latter gains intensity relative to the former. The 856.5 cm^{-1} band is also favored over the 854.0 cm^{-1} band upon dilution of the matrix to 0.5% Ar in Ne (*15*). We propose that Ar atoms are interacting directly with the CUO molecule, just as they do in the matrix of pure Ar, even in the most dilute matrix we used. We propose that the 856.5 and 854.0 cm^{-1} bands correspond to differing numbers of Ar atoms bonded to the CUO molecule.

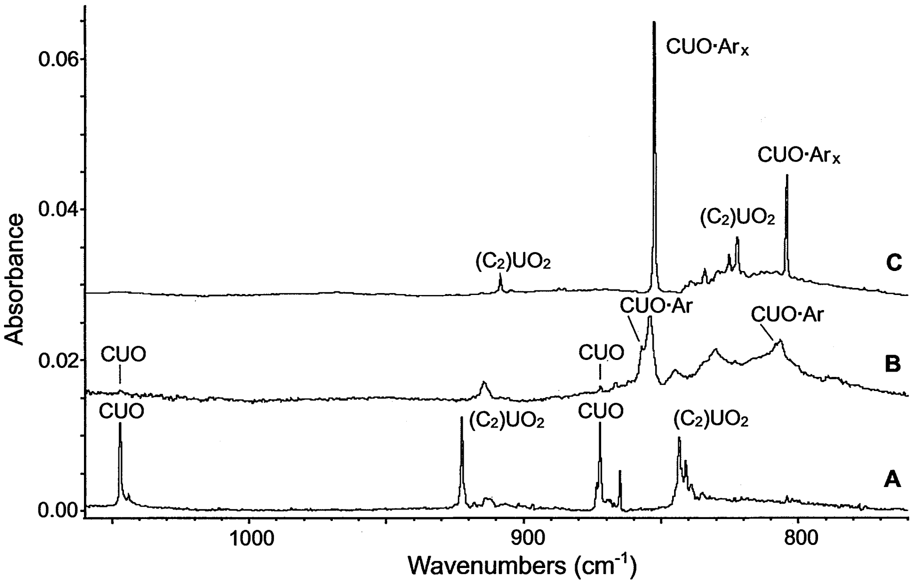


Fig. 1. Infrared spectra in the 1060 to 760 cm^{-1} region for laser-ablated U atoms codeposited with CO in excess noble gas. (**A**) Spectrum obtained when U atoms and 0.1% CO in Ne are deposited for 30 min, followed by full-arc photolysis (λ > 240 nm) and annealing at 10 K. (**B**) Spectrum obtained when U atoms, 0.1% CO, and 1% Ar in Ne are deposited for 30 min, followed by full-arc photolysis and annealing at 10 K. (**C**) Spectrum obtained when U atoms and 0.3% CO in Ar are deposited for 15 min, followed by full-arc photolysis and annealing at 35 K.

We performed relativistic DFT calculations on CUO·Ng using the Amsterdam Density Functional (ADF) code with the PW91 functional and very diffuse basis sets to circumvent the well-known difficulties of performing electronic structure calculations on noble gas systems (*16*, *17*). Calculations on CUO·Ar were carried out with the CUO molecule in its $^1\Sigma^+$ ($^1A'$) ground state and its low-lying $^3\Phi$ ($^3A''$) excited state, where the Greek state designations are for the linear ($C_{\infty v}$ symmetry) geometry of CUO, whereas the designations in parentheses are appropriate for the CUO·Ar molecule, which has C_s symmetry. We find that CUO·Ar is a planar molecule with a $^3A''$ ground state in which a bent CUO fragment (∠CUO = 166.5°) is bound to the Ar atom primarily through the U atom (Fig. 2). The U-Ar distance in the converged structure is 3.16 Å (*18*), which is smaller than the sum of the crystal radii of the two elements (3.25 Å) (*19*). The U-C stretching frequency of $^3A''$ CUO·Ar shows a much greater decrease relative to $^1\Sigma^+$ CUO than does the U-O stretch, which is consistent with a decrease in the U-C bond order in the triplet state relative to the singlet.

The calculated DFT vibrational frequencies for CUO·Ar are summarized in Table 2 and are compared to the experimental data and the calculated results for the $^3\Phi$ state of the isolated CUO molecule. The inclusion of the Ar atom in the complex results in improvement in the calculated values of the predominantly U-C and U-O stretching modes and of the two isotopic shift ratios relative to the calculated values of isolated $^3\Phi$ CUO. Further, because the Ar atom interacts most significantly with the U and C atoms, the U-C stretching frequency is affected much more than the U-O frequency relative to the isolated CUO molecule, which is consistent with the experimental observations. The absolute errors in the calculated stretching frequencies of CUO·Ar, 30 to 40 cm^{-1}, are significantly greater than the error in our calculated frequencies for $^1\Sigma^+$ CUO in a Ne matrix (*9*, *20*). The Ar-U stretching mode is predicted to occur at 85 cm^{-1}, which is outside the spectral window in which we can observe vibrations.

Figure 2 shows a slice through the calculated potential energy surfaces of the $^3A''$ ground state and $^1A'$ excited state of CUO·Ar as a function of the U-Ar distance. Several observations are relevant: (i) At long U-Ar

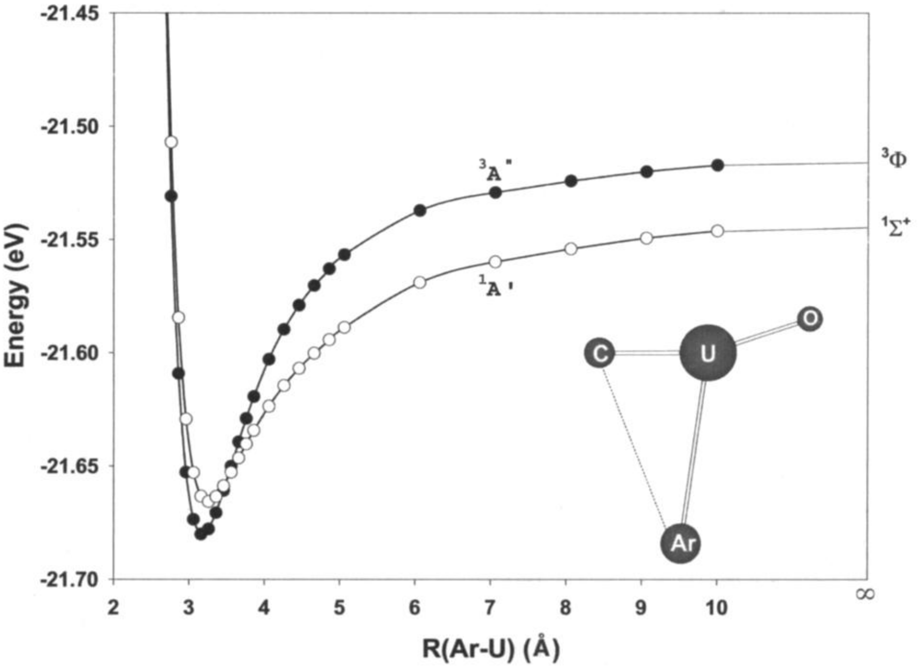


Fig. 2. Potential energy curves for the $^1A'$ and $^3A''$ states of CUO·Ar as a function of the U-Ar distance. The inset figure at lower right shows the optimized structure of the $^3A''$ state of CUO·Ar. The U-Ar bond length in this complex is 3.16 Å.

distances, the two states cross, with the singlet becoming the ground state, which is consistent with CUO in Ne matrices being essentially an isolated closed-shell molecule. (ii) Both the $^3\Phi$ and $^1\Sigma^+$ states of CUO are stabilized by interaction with an Ar atom, which is greater for the former to such an extent that the $^3A''$ component of the $^3\Phi$ state is stabilized below the $^1A'$ state. (iii) The $^3A''$ state of CUO·Ar lies 3.7 kcal/mol below Ar + CUO ($^3\Phi$ excited state) and 3.2 kcal/mol below Ar + CUO ($^1\Sigma^+$ ground state) (*21*). This degree of stabilization is significantly greater than that for dispersion forces and is comparable to the measured and calculated Ar-M bond dissociation energies for the other very few reported examples of neutral Ar-metal atom complexes (*22*), namely $ArW(CO)_5$ ($\leq$3 kcal/mol, measured) (*23–25*), ArBeO (6.7 kcal/mol, calculated) (*26*, *27*), and the Ar-metal-halide complexes ArCuX (11.3 kcal/mol, calculated for ArCuF) (*28*), ArAgX (5.6 kcal/mol, calculated for ArAgF) (*29*), and ArAuCl (11.2 kcal/mol, calculated) (*30*).

Orbital analysis of the calculations on $^3A''$ and $^1A'$ CUO·Ar indicates that, in both complexes, the Ar atom serves as a Lewis base that donates electron density into an empty U 6d orbital. This Lewis acid-base interaction is stronger for the $^3A''$ state for two reasons, both of which arise because the $^3A''$ state corresponds to the transfer of a U-C bonding electron into one of the nonbonding U 5fφ orbitals. First, because the U-C bond order is smaller in the triplet, the calculated U-C distance in $^3A''$ CUO·Ar (1.858 Å) is more than 0.1 Å longer than that in $^1A'$ CUO·Ar (1.752 Å). The longer U-C bond in $^3A''$ CUO·Ar leads to smaller repulsive Ar-C interactions as the Ar atom approaches the U atom. Second, the transfer of an electron into a U 5f orbital is an effective reduction of U(VI) to U(V). The expansion of the U 6d orbitals upon reduction leads to greater overlap and stronger interaction between the U 6d acceptor orbital and the Ar 3p donor orbital. Consistent with this model, the DFT calculations predict that the interaction of a Kr or Xe atom with CUO is stronger than that of an Ar atom: The stabilizations of the $^3A''$ ground states of CUO·Kr and CUO·Xe are 1.1 and 3.6 kcal/mol greater than that in CUO·Ar, respectively. The calculated U-Kr and U-Xe distances, 3.24 and 3.30 Å, respectively, are shorter than the sums of the crystal radii (3.41 and 3.58 Å, respectively).

In the matrices with a small amount of Ar in Ne, the bands due to CUO are broad doublets in which the lower-energy component is at nearly the same energy as the bands in the pure Ar matrix. Annealing the matrix or increasing the amount of Ar in the Ar/Ne matrices favors the lower-energy component of these doublets. These observations suggest that different CUO·Ar_x species are formed depending on the specific experimental conditions, a proposal that has precedent in other recent studies in noble gas matrices. Lorenz *et al.* presented evidence that Xe atoms "solvate" HXeBr and HXeCl even in Ne matrices with only small amounts of added Xe, and that this degree of solvation depends on Xe concentration and whether the matrix has been annealed (*31*). We have previously shown that the NUO molecule, formed via the reaction of U atoms and NO in solid Ne, is an isolated molecule before annealing, but that annealing allows aggregation of NUO and NO (*32*). To explore the notion of multiple CUO·Ar_x species further, we calculated the structures of CUO·Ar_x (x = 2 to 6) complexes. Our theoretical results provide strong support for the binding of multiple Ar atoms to a single CUO molecule. The calculated CUO-Ar binding energies increase and the stretching frequencies decrease as an increasing number of Ar atoms are attached to CUO. The binding of two or more Ar atoms continues to favor the triplet form of CUO, and the second and subsequent Ar atoms lead to much smaller changes in the calculated vibrational frequencies than does the first Ar atom; for example, we calculate that the C-U and U-O stretching frequencies in triplet C_{4v} CUO·Ar_4 are reduced only by 8 to 12 cm^{-1} relative to CUO·Ar. Thus, we propose that the 856.5 cm^{-1} band in Fig. 1B is probably due to CUO·Ar, whereas the low-energy component and the peaks in the pure Ar matrix in Fig. 1C are due to the binding of multiple Ar atoms to a single CUO molecule. We predict that CUO is in a triplet state regardless of how many Ar atoms are bonded to the molecule, and that the major change in the vibrational frequencies is due to the change in spin state from a singlet in isolated CUO to a triplet in CUO·Ar_x.

Table 2. Experimental and calculated frequencies (cm^{-1}) and isotopic shift ratios for the stretching frequencies of CUO and CUO·Ar.

Experimental			Calculated (relativistic DFT)		
ν_{exp}	$^{12}C/^{13}C$	$^{16}O/^{18}O$	ν_{calc}	$^{12}C/^{13}C$	$^{16}O/^{18}O$
	Ne matrix			*CUO* ($^1\Sigma^+$)	
872.2	1.0020	1.0554	874	1.0023	1.0549
1047.3	1.0361	1.0010	1049	1.0357	1.0019
				CUO ($^3\Phi$)	
			843	1.0127	1.0514
			902	1.0260	1.0052
	Ar matrix			*CUO·Ar* ($^3A''$)	
804.3	1.0196	1.0469	834	1.0126	1.0520
852.5	1.0188	1.0092	887	1.0261	1.0046

We believe that the experimental and theoretical data presented here make a strong case for the interactions between the U atom of CUO and the noble gas atoms to be considered weak chemical bonds. The strong Lewis acidity of CUO leads to an attractive interaction of 4 to 7 kcal/mol. The U-Ng bond distances are short, and the U-Ng interaction is strong enough to change the spin state of the CUO molecule. Because of its positive charge, the UO_2^{2+} ion, which is isoelectronic with CUO, should form even stronger bonds with noble gas atoms, which could lead to a growing number of complexes that contain direct noble gas–to–actinide bonds.

References and Notes

1. N. Bartlett, *Proc. Chem. Soc.* **1962**, 218 (1962).
2. H. H. Hyman, Ed., *Noble-Gas Compounds* (Univ. of Chicago Press, Chicago, 1963).
3. P. Pyykkö, *Science* **290**, 117 (2000).
4. K. O. Christe, *Angew. Chem. Int. Ed. Engl.* **40**, 1419 (2001).
5. L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, M. Räsänen, *Nature* **406**, 874 (2000).
6. N. Runeberg, M. Pettersson, L. Khriachtchev, J. Lundell, M. Räsänen, *J. Chem. Phys.* **114**, 836 (2001).
7. S. Seidel, K. Seppelt, *Science* **290**, 117 (2000).
8. W.-P. Hu, C.-H. Huang, *J. Am. Chem. Soc.* **123**, 2340 (2001).
9. M. Zhou, L. Andrews, J. Li, B. E. Bursten, *J. Am. Chem. Soc.* **120**, 9712 (1999).
10. R. G. Denning, *Struct. Bonding (Berlin)* **79**, 215 (1992).
11. T. J. Tague Jr., L. Andrews, R. D. Hunt, *J. Phys. Chem.* **97**, 10920 (1993).
12. L. Andrews, B. Liang, J. Li, B. E. Bursten, *Angew. Chem. Int. Ed. Engl.* **39**, 4565 (2000).
13. M. E. Jacox, *Chem. Phys.* **189**, 149 (1994).
14. Indeed, our calculations in which the Ar matrix is modeled with a dielectric continuum indicate that the $^1\Sigma^+$ state is more stable than the $^3\Phi$ state by 2.1 kcal/mol.
15. In a 0.2% Ar in Ne matrix, the dominant species is the isolated singlet CUO molecule (1074.2 and 872.2 cm^{-1}), although the 856.5 and 808.0 cm^{-1} bands are still present.
16. G. Frenking, D. Cremer, *Struct. Bonding (Berlin)* **73**, 17 (1990).
17. J. Lundell, G. M. Chaban, R. B. Gerber, *J. Phys. Chem. A* **104**, 7944 (2000).
18. Our preliminary calculations using the much more accurate coupled-cluster CCSD(T) method predict similar U-Ar distances of 3.30 Å and 3.21 Å for the singlet and triplet states, respectively.
19. The crystal radii of the elements are from M. J. Winter, WebElements (http://www.webelements.com/) (WebElements, Sheffield, UK, 2001).
20. When the Ar matrix surrounding CUO·Ar is modeled with a dielectric continuum, the calculated CUO·Ar frequencies are within 12 cm^{-1} of the experimental values.
21. The inclusion of spin-orbit coupling is expected to stabilize the $^3A''$ state of CUO·Ar more than it does the $^1A'$ state, thus increasing the U-Ar binding energy relative to the scalar relativistic results.
22. D. C. Grills, M. W. George, *Adv. Inorg. Chem.* **52**, 113 (2001).
23. J. R. Wells, E. Weitz, *J. Am. Chem. Soc.* **114**, 2783 (1992).

24. X.-Z. Sun, M. W. George, S. G. Kazarian, S. M. Nikiforov, M. Poliakoff, *J. Am. Chem. Soc.* **118**, 10525 (1996).
25. A. W. Ehlers, G. Frenking, E. J. Baerends, *Organometallics* **16**, 4896 (1997).
26. C. A. Thompson, L. Andrews, *J. Am. Chem. Soc.* **116**, 423 (1994).
27. A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **226**, 11 (1994).
28. C. J. Evans, M. C. L. Gerry, *J. Chem. Phys.* **112**, 9363 (2000).
29. ———, *J. Chem. Phys.* **112**, 1321 (2000).
30. C. J. Evans, A. Lesarri, M. C. L. Gerry, *J. Am. Chem. Soc.* **122**, 6100 (2000).
31. M. Lorenz, M. Räsänen, V. E. Bondybey, *J. Phys. Chem. A* **104**, 3770 (2000).
32. M. Zhou, L. Andrews, *J. Chem. Phys.* **111**, 11044 (1999).
33. We thank P. Pyykkö for helpful discussions. Financial support for this research was provided by the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy Office of Basic Energy Sciences (grant DE-FG02-01ER15135 to B.E.B.) and by NSF (grant CHE00-78836 to L.A.). We are grateful to the Ohio Supercomputer Center and the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory for generous grants of computer time.

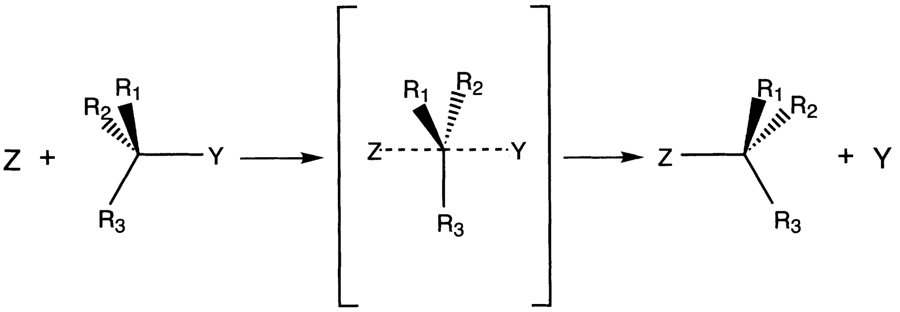
26 December 2001; accepted 13 February 2002
Published online 28 February 2002;
10.1126/science.1069342
Include this information when citing this paper.

Steric Effects and Solvent Effects in Ionic Reactions

Colleen K. Regan,[1] Stephen L. Craig,[2] John I. Brauman[3]*

Rates of S_N2 reactions of chloride ion with methyl- and *tert*-butyl–substituted chloroacetonitrile were measured by using Fourier transform–ion cyclotron resonance spectrometry to follow the isotopic exchange reaction. Barrier heights for these reactions indicate that steric effects in the gas phase are diminished relative to apparent steric effects in solution. We attribute the increased barrier in solution to a solvation effect. Monte Carlo simulations done using statistical perturbation theory confirm that steric hindrance to solvation contributes to S_N2 barriers in solution.

In the S_N2 nucleophilic displacement reaction, a nucleophile, Z (often negatively charged), reacts with a saturated carbon and displaces a leaving group, Y (Scheme 1). Increasing the size of the substituents, R, decreases the rate of the reaction by creating nonbonded interactions (steric effects) that raise the energy of the transition state.



Scheme 1.

The idea of a steric effect was first proposed by Hofmann (*1*, *2*) 130 years ago, but a quantitative understanding of this effect in the S_N2 reaction remains elusive (*3*, *4*). In solution, there is a dramatic reduction in rates and an increase in activation barriers associated with increasing alkyl substitution at the central carbon atom, regardless of the solvent. Early theoretical attempts using classical models to quantitatively understand the effect of structure on the energetics were mixed (*3*, *5*, *6*). Ingold's discussion of steric effects is the benchmark for other studies (*3*, *7*). This early work indicated that steric effects might not account for all of the barrier in solution (*8*), but only internal effects, such as the change in polar effects with substitution, were proposed to explain the rest of the barrier seen in solution (*7*). Solvation of transition states was considered equivalent in all cases. However, although structural interference clearly affects chemical behavior (*5*), we believe that steric effects in ionic reactions in solution are convoluted with solvent effects in a way that has not been explored.

Much of the barrier to the reaction of ions in solution is due to the desolvation of the nucleophile and the greater charge dispersal in the transition state (*3*, *9*, *10*). To isolate the role of solvation, however, it is necessary to look at thermoneutral reactions (*11*), such as isotopic exchange. Interpretation of an activation barrier for exothermic reactions requires a knowledge of the exothermicity and the intrinsic barrier of the reaction (*12*, *13*), thus making gas-phase versus solution interpretations difficult, at best.

Numerous gas-phase studies have shown that alkyl bulk does affect reactivity in the absence of solvent (*10*, *11*, *14*–*18*). Thermoneutral reactions of alkyl halides have proven to be too slow, so only exothermic reactions have been studied. Because alkyl bulk slows S_N2 reactions, often to a point where they are too slow to be measured accurately, there is no complete series of reactions with the prototypical types of substitution described in solution where the rates of, and barriers to, reaction have been determined accurately. The most extensively studied reaction, Cl^- + RBr, is nearly complete, but does not include the reactions where R = *tert*-butyl or neopentyl.

We report a gas-phase mass spectrometric study of thermoneutral S_N2 reactions of alkyl-substituted chloronitriles done to determine steric effects in different solvents in the absence of exothermicity and competing reactions. We show that differential solvation of the differently sized alkyl-substituted transition states plays a significant role in the increased barrier to reaction as the alkyl bulk is increased in solution (Fig. 1). Our Monte Carlo simulations with statistical perturbation theory on related thermoneutral reactions of alkyl chlorides confirm the hypothesis that differential solvation of transition states relative to each other contributes to the increased barriers seen in S_N2 reactions in solution for larger substrates.

Table 1. Reactions of Cl^- with alkylchloronitriles.

Chloronitrile	k_{exp} (molecules s^{-1} cm^{-3})	ΔE_{diff} (kcal mol^{-1})
2-Chloropropanenitrile, **1**	1.0×10^{-11}	–1.6
2-Chloro-3,3-dimethylbutanenitrile, **2**	1.6×10^{-12}	0.0

---

[1] Department of Chemistry, Bryn Mawr College, Bryn Mawr, PA 19010, USA. [2] Department of Chemistry, Duke University, Durham, NC 27708, USA. [3] Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA.

*To whom correspondence should be addressed. E-mail: brauman@stanford.edu