Table VI
Activation Parameters for ArCX/Alkene Additions[a]

carbene	tetramethylethylene $\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$-T\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	1-hexene $\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$-T\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
p-$CF_3C_6H_4CBr$	−1.6	−22	6.6	5.0	−0.19	−25	7.4	7.2
PhCBr	−2.1	−25	7.4	5.3	0.40	−26	7.7	8.1
PhCCl	−2.3	−28	8.3	6.0	0.51	−27	8.0	8.5
PhCF	−2.3	−28	8.3	6.0	0.71	−29	8.6	9.3
p-$CH_3OC_6H_4CF$	−0.4	−27	8.0	7.6	2.5	−29	8.6	11

[a] Data are from ref 55 and are calculated at 298 K. Units are kcal/mol for $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $T\Delta S^{\ddagger}$ and cal/(deg mol) for $\Delta S^{\ddagger}$.

species MeOCF and $(MeO)_2C$ are available from spectroscopically compatible precursors,[19,21] it should be possible to further probe enthalpy/entropy partition in carbenic cycloadditions. Indeed, dimethoxycarbene is sufficiently chromophoric to permit the measurement of absolute rate constants for its reactions,[21] so that activation parameters should soon be forthcoming.

Conclusion. The combined impacts of new carbene precursors, nanosecond kinetic methods, and realistic computations have greatly altered our detailed view of carbenic reactivity, while simultaneously integrating the newly emerging picture with the broader perspective of cycloaddition reaction theory. The entropic dominance manifested in carbene/alkene additions of very low $\Delta G^{\ddagger}$ is probably a feature of cycloaddition reactions in general, but we can see how the counterpoint between $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and carbenic structure underlies the classical reactivity pattern deduced from older, product-based studies. The continued application of sophisticated spectroscopic and computational methods to carbenic additions should now point toward the detailed mapping of their reaction surfaces.

I am enormously indebted to my associates, whose names appear in the references. Special thanks go to my colleagues, Prof. K. Krogh-Jespersen (Rutgers) and Prof. N. J. Turro and Dr. I. R. Gould (Columbia), whose close collaborations over the past eight years were essential to the work described herein. I also note with deep appreciation the central and continuing role played by my associates from Poland. Finally, I thank the National Science Foundation for its support of our efforts.

Chemical Reactions and Energy Transfer Processes of Electronically Excited Group IIB Metal Atoms: Full Collisions and Half-Collisions

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Received April 19, 1988 (Revised Manuscript Received October 3, 1988)

I. Introduction

A major goal of modern dynamics is to characterize elementary chemical reactions or energy-transfer processes in a "state-to-state" fashion. One would like to prepare initial reagents in a known (and preferably variable) set of quantum states and then determine the different rates at which various possible sets of product quantum states are formed. Such measurements must be "single-collision" in nature, because collisional thermalization of the prepared reagents before the process of interest takes place, or of the nascent product states before detection, decreases the content of the dynamical information sought. Preparation, collision, and detection must therefore occur at very low pressures or within very short periods of time at moderate pressures.

We have concentrated on studies of collisional processes involving electronically excited group II metal atoms, using a laser pump–probe technique.[1-12,14-17,20-27]

Bill Breckenridge was born on October 14, 1941. His first experience with research in chemistry was as an undergraduate at Kansas University with Sherry Rowland. After a year of graduate research in physical chemistry at Leeds University with Fred Dainton and Don Baulch on a Fulbright fellowship in 1964, he completed his Ph.D. degree in physical and inorganic chemistry at Stanford University in 1968 under the direction of Henry Taube. Following postdoctoral research in physical chemistry with Tony Callear at Cambridge University and Terry Miller at Bell Labs, in 1971 he joined the faculty at the University of Utah, where he is now Professor of Chemistry.

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In this Account, several examples of "full-collision" studies of energy disposal in chemical reactions or energy-transfer collisions of electronically excited metal atoms with simple reagents, most of which have been carried out in our laboratories, are described. The nature of this brief review prevents us from comprehensive consideration of the large body of excellent work by others in this field.[1,2,28-31] In our studies, the electronic state of the metal atom is selected, but there is a Boltzmann distribution (T = 400–500 K) of relative translational energies and of molecular reagent internal vibrational and rotational states. Especially for the predominantly high cross section processes described here, there is also a large range of possible collisional trajectories sampled, from "head-on" to "grazing" collisions, and with a range of geometrical orientations as well as electronic orbital alignments of the excited metal atom as the collision occurs. There is, of course, great interest in the dependence of the dynamics of simple collisional events on such factors.[32] Although other experiments with excited metal atoms, particularly those utilizing polarized laser sources or off-resonance excitation, are providing interesting relevant information, definitive interpretation of such results is often difficult.[28-31,33,34]

Our research group,[27] along with others,[16,23,24,35] has recently been developing "half-collision" techniques which not only are complementary to the laser pump-probe full-collision method developed in our laboratories[1,2] but also provide quite unique kinds of state selection. Initial experiments in this area were performed by Benoit Soep, Christophe Jouvet, and co-workers at Orsay, with whom we are pleased to have an on-going collaboration. The half-collision idea has been developed successfully in other areas as well, for example, by Wittig, Zewail, Janda, and co-workers.[35]

The essential idea of half-collision studies in our particular area of interest to really quite a simple one. Instead of exciting an electronic state of a metal atom and allowing the excited atom to collide with some reagent (atom or molecule), one can first gently *attach* the reagent to the metal atom and *then* excite the electronic state of the metal atom. Once activated, the system will subsequently undergo "half" a collision with the reagent. The "gentle" attachment of the reagent can be accomplished experimentally by expanding the metal vapor, the reagent, and a carrier gas through a nozzle into a resulting supersonic free jet. Because of the cooling in the jet, weakly bound one-to-one van der Waals molecules of the metal atom and the reagent can be synthesized for laser half-collision experiments in the collision-free portion of the supersonic jet.

There are several reasons why such half-collision studies are attracting increasing attention in the dynamics community:

i. The excited metal atoms can be created a certain distance from, and in some cases at a certain molecular geometry with respect to, the reagent. Because of the nature of the electronic excitation process (nuclear motion is quite slow compared to the motion of electrons), the initial conditions of half-collision experiments correspond closely to the nuclear geometry of the "cold" ground-state metal–reagent van der Waals complex.

ii. The excited metal atoms can be prepared with particular electronic orbital alignments with respect to the reagent. Even at the large metal–reagent distances corresponding to most ground-state van der Waals complexes, the energy differences between electronic symmetries of the excited-state metal atom with respect to the reagent are often sufficiently large that it is possible to select a *particular* symmetry by tuning the "pump" dye laser frequency a few wavenumbers away from the energy of the transition of the free atom. Dynamical differences, for example, between σ versus π orientations (i.e., along, versus perpendicular to, the metal–reagent axis) of an excited-state metal atom p orbital, can readily be observed.

iii. The relative translational velocity and the angular momentum of the collision can be partially selected. Because of the cooling in the free-jet expansion, the metal–reagent angular momentum and relative vibrational motion will be quite small. Since these two quantities correspond, respectively, to the translational orbital angular momentum and relative translational energy of "full" metal–reagent collisions, unique state selection can be achieved.

iv. Comparison of results of half-collision with those of full-collision experiments can be dynamically informative. Because of the state-selective nature of the half-collision experiments, comparison with analogous full-collision experiments can be very iluminating mechanistically.

In this Account, we first treat full-collision studies of electronic energy transfer using the laser pump–probe technique and discuss an equivalent half-collision study

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Table I.
Initial Distributions of Cd($^3P_{2,1,0}$) in Process 1, in Percent[6,26,27]

	product states (%)		
quencher	$^3P_2$	$^3P_1$	$^3P_0$
Xe	>90	<10[a]	<10[a]
Ar	>80	<16	<4
H_2	61 ± 2	36 ± 2	4 ± 1
N_2	55 ± 2	34 ± 2	11 ± 1
CO	56 ± 2	32 ± 2	12 ± 1
NO	49 ± 2	37 ± 2	14 ± 1
CH_4	76 ± 2	19 ± 2	5 ± 1
C_2H_6	67 ± 1	25 ± 1	8 ± 1
C_3H_8	65 ± 1	27 ± 1	8 ± 1
i-C_4H_{10}	56 ± 1	33 ± 1	11 ± 1
ethylene	37 ± 2	47 ± 2	16 ± 1
propylene	44 ± 3	42 ± 3	14 ± 1
isobutylene	57 ± 2	33 ± 2	10 ± 1
$2J + 1$	56	33	11

[a] Not detected.

completed recently in our laboratories. We then summarize a series of state-to-state, pump-probe studies of full-collision chemical reactions of excited states of group IIb metal atoms with H_2, HD, and D_2 to produce metal monohydride (monodeuteride) molecules. Finally, we describe a prototype half-collision experiment analogous to such reactive processes: the creation of, and reaction within, the Hg(6s6p$^3P_1$)–H_2 van der Waals molecule to produce HgH + H.

II. Electronic Energy Transfer

A. Full-Collision Studies. The following energy-transfer processes occur with very high cross sections for a variety of species X even though there is a spin change required:

$$\mathrm{Cd(5s5p^1P_1) + X \rightarrow Cd(5s5p^3P_{0,1,2}) + X} \qquad (1)$$

In the initial atomic state, the spin angular momentum is 0 (singlet), while in the final state, the spin angular momentum is 1 unit, leading to three states of different energy (triplet). The Cd($^1P_1$) state has 125.0 kcal/mol electronic energy, while the Cd($^3P_2$), Cd($^32P_1$), and Cd($^3P_0$) states have 91.0, 87.6, and 86.0 kcal/mol, respectively. Remarkably, even though there are also quite exothermic *chemical reaction* exit channels available in many cases which can occur in a *spin-allowed* fashion, process 1 usually predominates.[1,4,6,37,38]

Studies conducted in our laboratories[6] showed that the initial J-state distributions of Cd(^3P_J) varied dramatically with the identity of the quenching species X. Shown in Table I are the initial $^3P_2$, $^3P_1$, and $^3P_0$ percentages for a selected group of quenching species. If the atomic product states were populated solely on the basis of their $2J + 1$ electronic degeneracies, the $^3P_2$:$^3P_1$:$^3P_0$ percentages would be 56:33:11. From Table I, some molecules, in fact, do appear to produce the J states in just such an electronically statistical distribution, while other quenching species produce initial Cd(^3P_J) state distributions that are markedly *nonstatistical*.

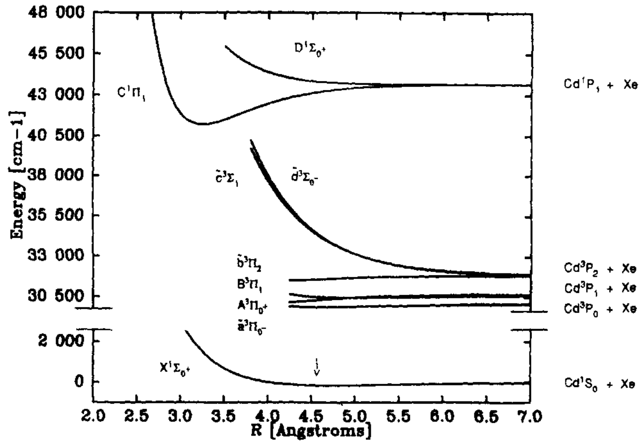

Figure 1. Estimated potential curves of the ground state and low-lying excited states of the CdXe molecule. The arrow indicates r_e for the CdXe($X^1\Sigma^+$) ground state.

For the simplest atomic cases, the exclusive product for Xe (and probably for Ar) is Cd($^3P_2$), the multiplet state highest in energy.[6,26,27] Shown in Figure 1 are estimates of the relevant CdXe diatomic potential curves constructed by utilizing spectroscopic information from various sources.[13,18,19,27,39–44] As can be seen, a collision of Cd($^1P_1$) with Xe can populate the bound CdXe($C^1\Pi_1$) state (the Π notation indicating that the p orbital on the Cd atom is *perpendicular* to the Cd–Xe axis). The repulsive CdXe($\tilde{c}^3\Sigma_1^+$) state (Σ notation indicating *parallel* p-orbital orientation) correlating with Cd($^3P_2$) + Xe crosses the CdXe($C^1\Pi_1$) curve, and the exclusive production of Cd($^3P_2$) in the deactivation of Cd($^1P_1$) by Xe can be explained by an $\Omega = 1$ spin–orbit induced curve crossing. Similar results for quenching of Ba(6s6p$^1P_1$) by the rare gases[26] are consistent with this mechanistic postulate.

For the molecular quenching species, the quenching of Cd($^1P_1$) to form the Cd(^3P_J) states occurs on multidimensional potential surfaces which are difficult to estimate, even qualitatively. The statistical 56:33:11 distributions observed for several quenchers could result either from Cd($^1P_1$)–X potential surfaces which cross all surfaces correlating with the Cd(^3P_J) states or from efficient intramultiplet mixing of the J states on the Cd(^3P_J)–X exit-channel portions of the potential surfaces.[1,6,17] Future half-collision experiments of the type described in the following section should provide mechanistic information which will lead to a better understanding of these remarkably efficient spin-forbidden electronic energy transfer processes.

B. Half-Collision Study of Cd($^1P_1$) Deactivation by Xe.

Excitation of CdNe, CdAr, and CdKr. When cadmium vapor from an oven source is expanded in the presence of Ne, Ar, or Kr through a nozzle into a su-

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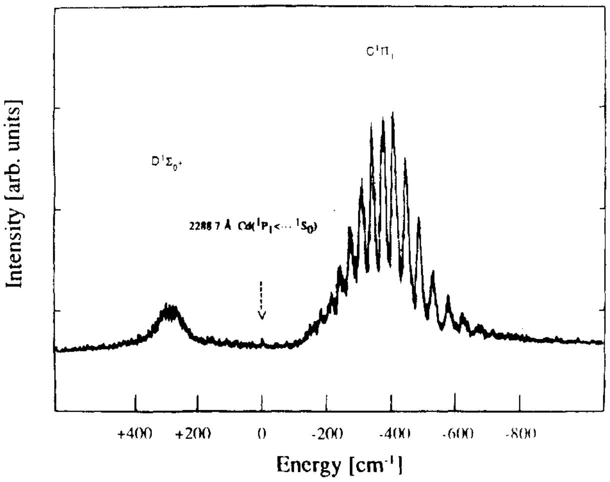

Figure 2. Action spectrum for the production of Cd($5s5p^3P_2$) from excitation of CdXe near the Cd($5s5s^1S_0 \rightarrow 5s5p^1P_1$) atomic transition.[27] A probe laser pulse, delayed by a few nanoseconds, is fixed onto the Cd($5s5p^3P_2 \rightarrow 5s6s^3S_1$) transition while the pump laser is scanned through the frequency region shown.

personic free jet, weakly bound ground-state Cd–RG molecules (RG = rare gas) are created and cooled to a few degrees Kelvin.[13,39,40] Laser-induced fluorescence spectra consisting of vibrational progressions are readily obtained to the red of the Cd($^1S_0$) → Cd($^1P_1$) atomic transition and have been identified as Cd–RG($X^1\Sigma^+$,v''=0) → Cd–RG($C^1\Pi_1$,v') excitations.[40] Wavelength-resolved bound-to-free emission spectra from each of the accessible upper vibrational states v' have enabled us to assign the upper-state vibrational quantum numbers and determine the Cd–RG($C^1\Pi_1$) potential curves and dissociation energies.[40] The curves are similar to the CdXe($C^1\Pi_1$) curve portrayed in Figure 1, in that the $C^1\Pi_1$ states are all much more strongly bound and have an equilibrium bond length much less than the corresponding $X^1\Sigma_0^+$ ground states.

When the excitation laser is tuned to the blue of the Cd($^1S_0$) → Cd($^1P_1$) atomic line, no molecular fluorescence is observed for CdNe, CdAr, or CdKr. But when a second (probe) laser pulse, delayed by only 4 ns, is fixed on an atomic transition for sensitive detection of Cd($^1P_1$) and the excitation laser is again scanned to the blue, continuous "action" spectra are obtained which are consistent with bound-to-free absorption from Cd–RG($X^1\Sigma^+$,v''=0) to repulsive portions of the very weakly bound Cd–RG($D^1\Sigma_0^+$) upper states, which then dissociate within 1 ps to form Cd($^1P_1$). (See Figure 1.)

Excitation of CdXe. In stark contrast to the CdNe, CdAr, and CdKr cases, careful attempts to obtain the analogous CdXe($X^1\Sigma_0^+ \rightarrow C^1\Pi_1$) laser-induced fluorescence spectrum resulted in no observable fluorescence when the excitation laser was tuned to the red of the atomic line.[27] However, pump–probe "action" experiments similar to those described above, in which the probe laser was tuned to detect Cd($^1P_1$), revealed a continuum to the blue indicative of the CdXe($X^1\Sigma_0^+ \rightarrow D^1\Sigma_0^+$) bound-to-free transition, showing that we were indeed making CdXe in high concentrations. We then attempted to measure pump–probe action spectra for Cd($^3P_2$) production, with good success.[27] Shown in Figure 2 is a Cd($^3P_2$) action spectrum obtained for CdXe. The Cd($^3P_2$) state is produced exclusively, since Cd($^3P_1$) or Cd($^3P_0$) could not be detected.[27]

The vibrationally relaxed spectrum observed to the red is very similar to the Cd–RG($X^1\Sigma_0^+$,v''=0) → Cd–RG($C^1\Pi_1$,v') laser-induced fluorescence spectra observed for RG = Ne, Ar, and especially Kr. The maxima represent vertical excitation of high vibrational levels v' of CdXe($C^1\Pi_1$) (see Figure 1), which instead of fluorescing undergo efficient predissociation to produce Cd($^3P_2$). Because Cd and Xe have several isotopes, the splitting due to accumulated vibrational energy differences for the isotopic molecules of high v' contributes to the observed broadening.[44] Extensive spectral simulations of the CdXe vibrational bands indicate, however, that an additional Lorentzian (Heisenberg) broadening component of 7 cm^{-1} is required to account for the vibrational band contours.[27] This is equivalent to a predissociation lifetime of 0.8 ps, or roughly one CdXe($C^1\Pi_1$) vibration. Thus the half-collision production of Cd($^3P_2$) is very efficient.

A surprising aspect of the Cd($^3P_2$) action spectrum (Figure 2), however, is the appearance of a continuum to the *blue* which is, within experimental error, indistinguishable from the Cd($^1P_1$) action spectrum in the same spectral region, attributed above to excitation to the repulsive portion of the CdXe($D^1\Sigma_0^+$) curve followed by immediate dissociation to Cd($^1P_1$). This observation was quite unexpected, and it appears that the mechanism is coupling between the CdXe($D^1\Sigma_0^+$) and CdXe($C^1\Pi_1$) electronic states during the approximately 1 ps transit time through the repulsive portion of the CdXe($D^1\Sigma_0^+$) curve (see Figure 1). Production of CdXe($C^1\Pi_1$) would in turn induce the efficient CdXe($C^1\Pi_1$) → CdXe($\tilde{c}^3\Sigma_1$) curve-crossing, yielding Cd($^3P_2$). The CdXe($D^1\Sigma_0^+$) coupling to CdXe($C^1\Pi_1$) can only be *rotationally* induced, but CdXe has a mean rotational angular momentum on the order of 15$\hbar$ even at 5 K.[27]

III. Chemical Reactions

A. Full-Collision Studies of the Reactions of Electronically Excited Metal Atoms with H_2, HD, and D_2.

The triplet ($nsnp^3P_1$) or singlet ($nsnp^1P_1$) states formed by exciting an s electron from the ($nsns^1S_0$) ground states of Mg, Zn, Cd, or Hg atoms are very reactive toward H_2 or other molecular hydrides.[1–3,5–7,11,12,14,15,17,20–22,37,38,45–47] In many cases, the primary initial product is the electronic ground state of the metal monohydride:

$$M(nsnp) + XH \rightarrow MH + X$$

This high reactivity appears to be due to particularly favorable conditions for *side-on* (insertive) attack of the H–H (or X–H) bond,[1,2,45–49] in contrast to the preference for *end-on* (abstractive) attack by such well-known reagents as ground-state halogen[50] or oxygen[51] atoms. For side-on approach to H_2, not only is there good overlap of the singly occupied pπ orbital of the excited metal atom with the empty antibonding σ^* H–H orbital, but the filled σ orbital of the H–H single bond can also

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overlap with the half-empty s orbital on the metal atom.[1,2,47,48] Ab initio theoretical calculations in our research group, as well as by others, of BeH_2, MgH_2, and HgH_2 potential surfaces are quite consistent with this mechanistic idea.[48,49,52]

A series of state-to-state studies of the dynamics of these reactions[11,14,15,20,21,53] show that the excited metal atoms M(*nsnp*) insert into the H–H bond to form very short lived H–M–H intermediates which subequently decompose to MH + H products. As an example, we describe in more detail our studies of the reactions of $Zn(4s4p\,^3P_1)$ with H_2, HD, and D_2:[21]

$$Zn(^3P_1) + H_2 \rightarrow ZnH(v,N) + H \qquad (2)$$

$$Zn(^3P_1) + HD \rightarrow ZnH(v,N) + D \qquad (3)$$

$$Zn(^3P_1) + HD \rightarrow ZnD(v,N) + H \qquad (4)$$

$$Zn(^3P_1) + D_2 \rightarrow ZnD(v,N) + D \qquad (5)$$

By exciting $Zn(^3P_1)$ with a "pump" dye laser pulse in a Zn/He vapor stream to which has been added H_2, HD, or D_2 and detecting ZnH or ZnD using fluorescence from the ZnH (ZnD) $A^2\Pi \leftarrow X^2\Sigma^+$ transition induced by a tunable "probe" dye laser pulse delayed by a few nanoseconds, it has been possible to determine the complete initial vibrational and rotational quantum state distributions (v,N) of the above four isotope reactions.[21]

For reactions 2–5, energy is *not* deposited preferentially into vibrational motion of the ZnH (ZnD) products. The $v = 0$ state of ZnH (ZnD) is the most highly populated vibrational quantum state in each reaction, and the population of higher vibrational states drops off as v increases. Similar results have been obtained for the analogous reactions of *nsnp* excited states of Hg, Cd, and Mg.[11,14,15,20,53] This indicates relatively "late" release of energy and is consistent with decomposition of an H–Zn–H intermediate in which one Zn–H bond distance remains similar to that of the final ZnH product molecule as the other Zn–H bond breaks.

The most striking results, however, involve the detailed *rotational* quantum state distributions of the $ZnH(v{=}0,1)$ and $ZnD(v{=}0,1)$ products of reactions 2–5. Shown in Figure 3 are the $ZnH(v{=}0)$ and $ZnH(v{=}1)$ initial rotational quantum state distributions from reactions 2 and 3. The high degree of rotational excitation is consistent with the decomposition of a nonlinear H–Zn–H insertion intermediate. The surprising aspect of the results in Figure 3, however, is that the $ZnH(v{=}0)$ and $ZnH(v{=}1)$ rotational distributions are *very similar* for HD versus H_2 as reactants (reactions 2 and 3). Thus the distribution of rotational energy of the $ZnH(v{=}0,1)$ products does not change even when the mass of the leaving atom is *doubled*, from H to D.[21] This unusual result has also been observed for the analogous reactions of $Cd(5s5p\,^3P_1)$ and $Hg(6s6p\,^3P_1)$, with H_2, HD, and D_2 to form the $v = 0$ metal monohydrides and monodeuterides.[15,53]

Early *impulsive* (sudden) release of energy by H–H (H–D) bond breaking in an MH_2 intermediate (M = Hg, Cd, Zn) can be ruled out, since the "push-off" of a light H–M rotor from a heavier D atom would lead to more rotational excitation than that from a light H atom.[54] We believe that in these cases the H–H bond has already been broken, and that the rotational energy results from H–MH bond-breaking pathways in which the electronic potential energy varies with both the H–M bond distance and the H–MH bond *angle*, i.e., an anisotropic exit-channel potential surface.[21,22] The final rotational angular momentum of the MH product will equal (but be vectorially opposed to) the angular momentum of the H + MH fragments as they fly apart. In the HgH_2 case, recent ab initio calculations[49] of the strongly bent $^3B_2$ ($^3A'$) state of HgH_2, which correlates with $Hg(^3P_1) + H_2$ (and is the state corresponding to the molecular orbital interactions described qualitatively above), show just this kind of potential surface anisotropy in the H–HgH exit-channel geometries which lead adiabatically to ground-state HgH + H products.

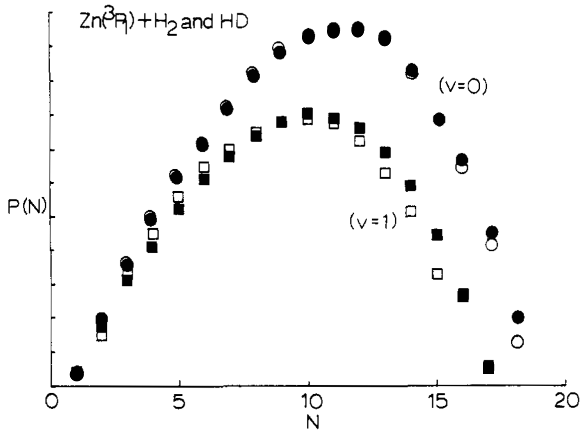

Figure 3. The initial rotational quantum state distributions of ZnH produced in the reactions of $Zn(4s4p\,^3P_1)$ with H_2 and HD (reactions 2 and 3, respectively).[21] Open circles and squares, H_2; filled circles and squares, HD. Maximum *N* energetically allowed for $v = 0$ is $N = 24$; for $v = 1$, $N = 19$. Ratios of $v = 0$ to $v = 1$ to $v = 2$ are 1.0:0.7:(<0.2).

Simple classical trajectory calculations[22] on model potential surfaces designed to mimic such anisotropy as the H–M–H(D) species dissociate have in fact shown that similar MH product rotational state distributions can result from D-leaving and H-leaving trajectories. Further confirmation of this speculative mechanism will require good theoretical full-collision dynamical studies on realistic potential surfaces, but our preliminary results are certainly intriguing.

B. Prototype Half-Collision Study of the $Hg(^3P_1)$–H_2 Reaction. In the final portion of this Account, we describe an elegant chemical reaction half-collision experiment[16,23,24] which should serve as a prototype for similar studies which will be attempted in the future. The work was carried out at the Laboratoire de Photophysique Moleculaire at Orsay by B. Soep and C. Jouvet, and I had the great pleasure of participating in the analysis of the results when I was on sabbatical leave. When Hg vapor, H_2, and He are expanded through a nozzle into a supersonic free jet, the ground state $Hg–H_2$ van der Waals complex is created and cooled to a few degrees Kelvin. Since the $Hg–H_2$ binding energy is only 35 cm^{-1} and the $Hg–H_2$ bond distance is quite large (4.0 Å), the H_2 molecule is unhindered and has a random distribution of geometric

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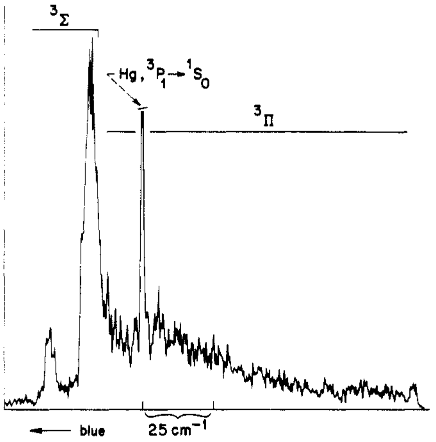

Figure 4. Action spectrum for the production of $HgH(X^2\Sigma^+, v''=0)$ from excitation of $Hg-H_2$ near the $Hg(6s6s^1S_0 \rightarrow 6s6p^3P_1)$ atomic transition.[16] A probe laser pulse, delayed by a few nanoseconds, is fixed onto a rotational line of the $HgH(X^2\Sigma^+, v''=0) \rightarrow HgH(A^2\Pi_{1/2}, v'=0)$ transition while the pump laser pulse is scanned through the frequency region shown. Regions of the spectrum thought to be due to excitation of the $^3\Sigma(B1)$ or $^3\Pi(A0^+)$ states of $Hg-H_2$ correlating asymptotically with $Hg(6s6p^3P_1) + H_2$ are indicated.

orientations with respect to the Hg atom.[24] The $Hg-H_2$ van der Waals molecule is also cooled *rotationally* to a few degrees Kelvin and has a most probable rotational angular momentum of only $1\hbar$ or $2\hbar$.

The ground-state Hg–Ne van der Waals molecule has a binding energy of 37 cm^{-1}, essentially identical with that of the $Hg-H_2$ molecule.[16,43] Rotationally resolved spectra of HgNe near the $Hg(6s6s^1S_0) \rightarrow Hg(6s6p^3P_1)$ atomic transition at 2537 Å show two electronic transitions, one to the blue and one to the red of the atomic line.[16,43] The upper states of the "red" and "blue" transitions were shown to be the $A(0^+)$ and B(1) states (Hund's case c notation), respectively, which correlate asymptotically to $Hg(^3P_1)$ + Ne. (See Figure 1 for portions of the analogous CdXe states.) The $A(0^+)$ state corresponds to a pure Π state with the p orbital of the excited mercury atom aligned perpendicular to the bond axis.[16,55] The B(1) state, on the other hand, has partial Σ and partial Π character at long range, but is sometimes referred to as a "$^3\Sigma$" state since it is much less strongly bound.[16,55]

Because the $Hg-H_2$ molecule is similar to the Hg–Ne molecule, tuning a dye laser pulse a few wavenumbers to the red and to the blue of the atomic transition should excite $Hg-H_2$ to analogous $Hg-H_2(A0^+)$ and $Hg-H_2(B1)$ states, respectively. However, fluorescence excitation spectra of $Hg-H_2$ in this region reveal only an absorption continuum which has a sharp onset 40 cm^{-1} to the *blue* of the atomic line which *decreases* in intensity to the blue.[16] Experiments in which a second probe dye laser pulse is fixed on a transition suitable for detection of free $Hg(^3P_1)$ atoms show that this fluorescence is due to production and subsequent fluorescence of $Hg(6s6p^3P_1)$ because $Hg-H_2$ is excited to $Hg-H_2(B1)$ at energies above its dissociation limit.

However, when the second probe laser is tuned onto a rotational line of the $^2\Sigma^+(v''=0) \rightarrow {}^2\Pi_{1/2}(v'=0)$ transition for detection of the HgH molecule, and the first laser is again scanned through the spectral region near the 2537-Å atomic line, an action spectrum is obtained, which is displayed in Figure 4. In the region to the blue, where $HgH_2(B1)$ should be excited, there are indeed two peaks which can be assigned to the (0,0) and (1,0) vibrational bands of this transition. In the region to the red, where $HgH_2(A0^+)$ should be excited, there is only a very broad continuum. It appears, then, that excitation of the $Hg(^3P_1)-H_2$ states causes chemical reaction to produce HgH + H, but by two quite different mechanisms.

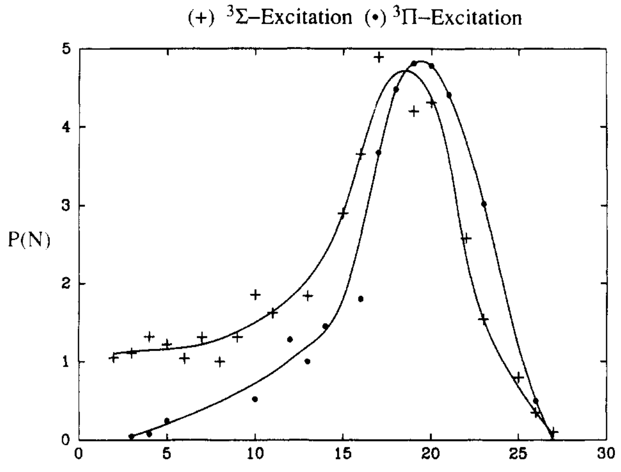

Figure 5. Rotational distributions of $HgH(X^2\Sigma^+, v''=0)$ product obtained by (a) fixing the pump laser 18 cm^{-1} to the blue of the $Hg(6s6s^1S_0 \rightarrow 6s6p^3P_1)$ atomic line to the maximum in the action spectrum shown in Figure 4 (plus signs; this results in excitation of the $^3\Sigma(B1)$ state of $Hg-H_2$) and (b) fixing the pump laser 25 cm^{-1} to the red of the atomic line as shown in Figure 4 (dots; this results in excitation of the $^3\Pi(A0^+)$ state of $Hg-H_2$).[16,23]

Excitation of the $HgH_2(A0^+)$ state ($^3\Pi$) produces HgH + H rapidly. From the spectral broadening of 50 cm^{-1}, the reaction must occur within less than 0.2 ps. On the other hand, excitation of the $HgH_2(B1)$ state ($^3\Sigma$) produces HgH + H, but in a relatively *slow* process. From the maximum broadening necessary to simulate the action spectra rotational band contours, the reaction time must be *greater* than about 4 ps.[24] There is apparently a potential barrier to chemical reaction,[49] and the $Hg-H_2(B1)$ state ($^3\Sigma$) is thus trapped momentarily in its shallow (20 cm^{-1}) van der Waals well for dissociation to $Hg(^3P_1)$, and behind the chemical activation barrier to form HgH + H. The HgH + H products *are* eventually produced, however, and one possibility[16,56] is that there is a weak coupling between the B(1) and $A(0^+)$ electronic states, perhaps induced by $Hg-H_2$ rotational motion or internal H_2 rotation for the 75% of the molecules with $J = 1$ (ortho) H_2. The other obvious possible mechanism is tunneling of the light H atom through the activation barrier.[16]

Relevant to these considerations, two more sets of data were obtained in this study:[16] the initial rotational quantum state distributions of $HgH(v=0)$ when the pump laser was tuned, and fixed in frequency, to the blue (at the maximum of the (0,0) band) to excite $HgH_2(B1)$, and to the red of the atomic line by 25 cm^{-1} to populate the $HgH_2(A0^+)$ state. The results are shown in Figure 5. As can be seen, the $A(0^+)$ excitation ($^3\Pi$) produces a sharply peaked rotational distribution, consistent with the formation and decomposition of an

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H-HgH intermediate on an anisotropic exit-channel potential surface.

For excitation of the B(1) state ($^3\Sigma$) of Hg-H_2, the major portion of the HgH(v=0) rotational state distribution (see Figure 5) is very similar to that from $^3\Pi$ excitation, consistent with the B(1) to A(0^+) *rotational coupling* mechanism,[16,56] but there is a small yield of HgH(v=0) with low rotational quanta. Such low rotational energy is more consistent with an abstraction mechanism (linear Hg-H-H) and could be due to tunneling since the tunneling probability would be greatest for linear geometries, where one H atom is closest to the Hg atom. Detailed studies involving excitations of the van der Waals molecules Hg-H_2(para), Hg-D_2, and HgHD would be very informative.

Finally, it is interesting to note that the rotational state distribution of HgH(v=0) produced in the full-collision reaction of Hg($^3P_1$) with H_2 near room temperature is *very similar* to that for the HgH_2(A0^+) ($^3\Pi$) half-collision distribution shown in Figure 5.[16,53] This indicates that the energy release process in the two cases is *essentially the same*: i.e., due to decomposition of H-HgH formed by facile, insertive Π attack of the H-H bond by Hg($^3P_1$). Because the full-collision process has a large cross section (25 Å^2),[1,2] grazing collisions with initial angular momentum on the order of 15$\hbar$ must *dominate*, in contrast to the half-collision case, where the initial angular momentum is nearly 0. There is no dynamical tendency, therefore, for initial orbital angular momentum to be converted to rotational angular momentum of the HgH(v=0) product, consistent with our view that *exit-channel* (chemical) potential forces are mainly responsible for the rotational energy of the diatomic product in the thermal reaction.

I am grateful to all the students, postdoctoral fellows, and visiting professors who have contributed to the research in our laboratories at the University of Utah over the years, particularly to David Funk and Jiang-Hua Wang, whose recent Ph.D. research has been highlighted in this article. I would also like to acknowledge all my collaborators at Orsay, especially Benoit Soep, Christophe Jouvet, and Marie-Christine Duval, for sharing their creative approaches to this entire research area. Finally, I am grateful to the National Science Foundation for continuing financial support of our research program at the University of Utah as well as our collaborative research effort with French scientists at Orsay.

1,3,5-Tris(dialkylamino)benzenes: Model Compounds for the Electrophilic Substitution and Oxidation of Aromatic Compounds

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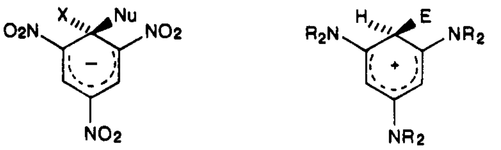
Received May 10, 1988 (Revised Manuscript Received October 3, 1988)

Anionic σ complexes have been known and extensively studied as intermediates of nucleophilic aromatic substitution since the beginning of the century.[1] In a paper that still makes fascinating reading, Meisenheimer describes the formation and isolation of anionic σ complexes by reaction of picryl ethers with potassium alkoxides. Structural proof is derived from the fact that identical σ complexes are obtained from methyl 2,4,6-trinitrophenyl ether with potassium ethoxide, and from ethyl 2,4,6-trinitrophenyl ether with potassium methoxide.[2] Cationic σ complexes (Wheland intermediates), on the other hand, had been characterized or isolated only in a few cases,[3] despite the ubiquitous implication of electrophilic aromatic substitution in synthesis. Such cationic σ complexes were expected to be stabilized best by three amino substituents, in meta positions relative to each other,[4] in analogy to the stabilization of anionic σ complexes by three meta-oriented nitro groups (Scheme I).

Scheme I[a]



anionic σ complexes (Meisenheimer complexes)

catonic σ complexes (Wheland intermediates)

[a] Nu = nucleophile, E = electrophile.

Neither 1,3,5-triaminobenzene itself nor its N-monosubstituted derivatives can serve as model substrates for arene reactions: these compounds exist, at least in part, in the form of the nonbenzenoid tautomers,[5] and

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