electronic changes are what would be expected based on SCF-$X\alpha$-SW calculations of the bulk ZnO states,[74] noting that even in the bulk, the π overlap between the zinc $3d^{10}$ electrons, which are greatly stabilized because of the closed-shell configuration, and the oxide $2p_{x,y}$ orbitals is very small (only 8% of the electron density is on the oxides for the $5t_2$ state), whereas the σ interaction between the zinc 4s and 4p and the oxide $2p_z$ is much larger, particularly for the $6a_1$ state.

This geometric and electronic structure picture of CO on ZnO has implications concerning its reactivity, in particular with respect to the synthesis of methanol. The polarized molecule has a strengthened CO bond, initially making C–O bond rupture less probable, but making the molecule susceptible to heterolytic attack by dissociated H_2, which is known to adsorb as Zn–H^- and OH^+.[75,76]

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Studies of Energy-Transfer and Electron-Transfer Processes Involving the $^3A_{2u}$ Excited States of Binuclear Rhodium Isocyanide Complexes

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Abstract: The lowest electronic excited states of $Rh_2(br)_4^{2+}$ (br = 1,3-diisocyanopropane) and $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) are relatively long-lived emissive triplets ($^3A_{2u}$). The $^3A_{2u}$ lifetimes in acetonitrile are 8.5 ± 0.5 μs for $Rh_2(br)_4^{2+}$ and 25 ± 5 ns for $Rh_2(TMB)_4^{2+}$ (21 °C). The triplet energy of $Rh_2(br)_4^{2+}$ has been estimated to be about 39 kcal/mol (~1.7 eV, ~730 nm) from energy-transfer quenching experiments. The $^3A_{2u}$ excited states of $Rh_2(br)_4^{2+}$ and $Rh_2(TMB)_4^{2+}$ undergo electron-transfer reactions with oxidative and reductive quenchers. Reductive quenching by *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), and oxidative quenching by paraquat (PQ^{2+}) have been studied in detail. In methanol solution, $Rh_2(br)_4^{2+}$* ($^3A_{2u}$) reacts with TMPD to give $Rh_2(br)_4^+$ and $TMPD^{+\cdot}$ (k_b, the back-reaction rate constant, is 1×10^9 M^{-1} s^{-1}); similarly, $Rh_2(TMB)_4^{2+}$* ($^3A_{2u}$) reacts with TMPD to give $Rh_2(TMB)_4^+$ and $TMPD\cdot^+$ ($k_b = 1.4 \times 10^9$ M^{-1} s^{-1}). Oxidation of $Rh_2(TMB)_4^{2+}$* ($^3A_{2u}$) by PQ^{2+} in methanol gives $Rh_2(TMB)_4^{3+}$ and $PQ\cdot^+$ ($k_b = 2.2 \times 10^8$ M^{-1} s^{-1}; $\mu = 1.95 \times 10^{-2}$ M). One-electron oxidation of $Rh_2(br)_4^{2+}$* ($^3A_{2u}$) by PQ^{2+} is observed, but the kinetics of the back-reaction are complex, owing to competing oligomerization processes.

Introduction

For several years we have been investigating the photochemistry of polynuclear metal complexes.[2-8] Part of our work has centered on the reduction of protons to hydrogen by solar irradiation of polynuclear complexes in homogeneous solutions.[3-7] One discovery of note in this area is that 546-nm irradiation of $Rh_4(br)_8^{6+}$ (br = 1,3-diisocyanopropane) in concentrated hydrohalic acids results in clean conversion to $Rh_2(br)_4X_2^{2+}$ (X = Cl, Br) and H_2. Our studies of the mechanism of this photoreaction suggest that a cluster cleavage process ($Rh_4^{6+} + h\nu \rightarrow Rh_2^{4+} + Rh_2^{2+}$; $Rh_2^{2+} + H^+ + \Delta \rightarrow {}^1/_2Rh_4^{6+} + {}^1/_2H_2$) is involved.[7] Unfortunately, the quantum yields for the overall photoreaction are low.

Our recent work on the photochemistry of polynuclear rhodium isocyanides has taken a somewhat different direction. We have decided to explore the redox chemistry of the long-lived (8.5 μs in CH_3CN solution)[8] triplet excited state ($^3A_{2u}$) of $Rh_2(br)_4^{2+}$. The photoredox chemistry of $Rh_2(br)_4^{2+}$ should be as rich as

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that[9-19] of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine), with the added advantage of a built-in cluster that should facilitate the multielectron steps required in solar energy storage reactions.

In this paper we report the results of energy-transfer and electron-transfer quenching experiments involving the $^3A_{2u}$ excited state of $Rh_2(br)_4^{2+}$ as well as related studies of the triplet excited state of $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane).[3] We have found that the Rh_2^+ and Rh_2^{3+} redox levels of these systems can be produced by electron-transfer reactions involving the Rh_2^{2+} excited states.

Experimental Section

Materials. Rhodium complexes (recrystalization solvents) were prepared by procedures given previously: $[Rh_2(br)_4](BPh_4)_2$ (acetonitrile);[8] $[Rh_2(br)_4](F_3CSO_3)_2$;[7] $[Rh_2(TMB)_4](PF_6)_2$ (acetonitrile);[20] $[Rh_2(TMB)_4](F_3CSO_3)_2$ (absolute ethanol).[7] Paraquat (PQ^{2+}) chloride (methyl viologen hydrate) was obtained from Aldrich. The $CF_3SO_3^-$ (triflate or TfO^-) salt was prepared by metathesis with AgTfO in methanol and, after removal of AgCl by filtration, was precipitated by addition of toluene. *N*-Methylnicotinamide tetrafluoroborate was prepared by metathesis of the iodide with $AgBF_4$ in methanol; after removal of AgI by filtration, the compound was precipitated by addition of ether and recrystallized from methanol/ether. The iodide salt was prepared by refluxing methyl iodide and nicotinamide in methanol for 2 h in the dark; it was recrystallized five times from methanol/ether. The iodide salt of 4-carbomethoxy-*N*-methylpyridinium was prepared similarly. From the iodide salt the tetrafluoroborate salt was prepared by metathesis with $AgBF_4$ in acetonitrile; after AgI was removed by filtration, the compound was precipitated by addition of ether and recrystallized from acetonitrile/ether. *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine (TMPD) from Aldrich was vacuum-sublimed twice and was stored under argon at −20 °C in the dark. 1,4-Diazabicyclo[2.2.2]octane (DABCO) from Aldrich was recrystallized in absolute ethanol twice, vacuum dried, and then vacuum-sublimed. Dimethylaniline (DMA) from Aldrich was vacuum-distilled and stored under argon at 5 °C in the dark. Both acetonitrile (Burdick and Jackson) and methanol (Aldrich) were spectrograde quality.

Equipment. Conventional flash photolysis was performed on an apparatus constructed at Caltech. The apparatus consists of a Xenon Corporation N851C flashlamp fired by a Model 457 micropulser (energy = 36–100 J/flash, $\tau_{1/2} \approx 5$ μs). The sample was placed in a 15-cm path length Pyrex cell that was filtered (Corning glass filters) to isolate appropriate spectral regions. The monitoring beam was the output of a DC quartz halogen lamp; detection employed an Oriel 7240 $^1/_4$ meter monochromator and a Hamamatsu R928 photomultiplier. The signal was displayed on either a Tektronix 549 storage oscilloscope with Type W plug in or on a Hewlett-Packard 7005B X-Y recorder after storage in a Biomation 805 transient waveform recorder.

Phosphorescence lifetime and nanosecond flash photolysis experiments were performed with a nitrogen laser/pumped dye laser system at Santa Cruz, CA, as described previously.[8] Excitation wavelengths (nm) were 337, 510 (dye = coumarin 500), 550 (coumarin 495), 580 (rhodamine 6G), and 610 (rhodamine B). The detection employed a McKee-Peterson 0.45-m monochromator and an EMI D279 photomultiplier (S-20 response). The photomultiplier output was displayed on either a Tektronix 466 storage oscilloscope or a Biomation 6500 transient waveform recorder coupled to a Mosley 135 X-Y recorder.

Table I. Energy-Transfer Quenching of $Rh_2(br)_4^{2+*}$ ($^3A_{2u}$) in CH_3CN Solution at 21 °C

quencher	E_t[a]	k_q, M^{-1} s^{-1}
azulene	30.9	6.25×10^9
9,10-dichloroanthracene	40.4	7.25×10^8
anthracene	42.7	3.4×10^6
trans-stilbene	~50	$\leqslant 4.0 \times 10^5$

[a] Triplet energies (E_t) in kilocalories per mole are from: Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

Procedures. Emission lifetimes were determined for the quenching of the $Rh_2(br)_4^{2+}$ triplet state by measuring the emission signal at 800 nm. In all cases (except DABCO, where it was necessary to use a high concentration of quencher) linear Stern–Volmer quenching kinetics were followed: $\tau^0/\tau = 1 + k\tau^0[Q]$. Kinetics of the back-reaction between photogenerated products was measured in conventional flash photolysis experiments; second-order kinetic behavior was deduced only when the second-order plot was linear for at least 3 half-lives.

All samples were freeze/pump/thaw degassed three times to a final pressure of less than 10^{-3} torr.

Results and Discussion

Lifetimes of Excited States. The $^1A_{1g} \rightarrow {}^1A_{2u}$ $[1a_{2u}(d_{z^2}) \rightarrow 2a_{1g}(p_z, \pi^*br)]$ absorption in the spectrum of $Rh_2(br)_4^{2+}$ peaks at 553 nm (ϵ = 14 500 M^{-1} cm^{-1}) in acetonitrile solution.[4,8,20] Excitation (550 nm) results in fluorescence (λ_{max} = 656 nm, τ < 2 ns) and a longer lived transient absorption (τ = 8 ± 4 μs).[8] By using a nitrogen pumped dye laser as the excitation source, we have observed emission at 800 nm from $Rh_2(br)_4^{2+}$ in acetonitrile, and we believe this to be emission from the state that is responsible for the aforementioned transient absorption. The 800-nm emission lifetime is 8.5 ± 0.5 μs for $Rh_2(br)_4^{2+}$ in acetonitrile at 21 °C. Similarly, for $Rh_2(TMB)_4^{2+}$ in acetonitrile, we have observed fluorescence (λ_{max} = 614 nm, τ < 2 ns),[4b] a second emission (λ_{max} = 770 nm, τ = 25 ± 5 ns), and a transient absorption (λ_{max} = 470 nm, τ = 30 ± 5 ns). Thus, each of these two binuclear rhodium complexes has two photochemically important electronic excited states ($^1A_{2u}$ and $^3A_{2u}$).[4b,8,21] In each case the longer lived state presumably is $^3A_{2u}$.

Energy Transfer. Since the fluorescence quantum yield is 0.056 for $Rh_2(br)_4^{2+}$ (0.046 for $Rh_2(TMB)_4^{2+}$) in acetonitrile at room temperature,[3b] the remaining 94% of the deactivation of $^1A_{2u}$ must proceed either by intersystem crossing to $^3A_{2u}$ or by internal conversion to the ground state ($^1A_{1g}$). In our previous work, we estimated that $\phi_{isc} > 0.8$ for $Rh_2(br)_4^{2+}$; this value comes from measurements of the transient bleaching at 553 nm during the period $^3A_{2u}$ absorbs, as observed by nanosecond flash photolysis.[8] Thus most, if not all, of the nonfluorescent deactivation of $^1A_{2u}$ goes by intersystem crossing. Also, in common with the behavior of triplets of aromatic organic molecules,[22] we have observed that the $^3A_{2u}$ state is quenched by triplet–triplet energy transfer. The results of these experiments are set out in Table I.

The quenching rate constant is diffusion controlled for $Rh_2(br)_4^{2+*}$ ($^3A_{2u}$)/azulene (E_t = 30.9 kcal/mol); however, the rate constant drops sharply for quenchers with E_t above 40 kcal/mol. It is well established that energy transfer that is exothermic by more than a few kilocalories per mole occurs at the encounter rate limit, but when E_t(quencher) ≈ E_t(donor), the rate constant is very sensitive to the relative energies of the reactants.[23] From the data obtained we estimate E_t for $Rh_2(br)_4^{2+*}$ ($^3A_{2u}$) to be 39 ± 2 kcal/mol (~1.7 eV, ~730 nm). This value is consistent with the spectroscopic results: the λ_{max} of phosphorescence is 800 nm

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Table II. Electron-Transfer Quenching of $Rh_2(br)_4{}^{2+*}$ ($^3A_{2u}$) in CH_3CN Solution at 21 °C

quencher	k_q, $M^{-1}\ s^{-1}$	$E°(+/0)$, V vs. SCE
DMA	$<1 \times 10^5$	0.71^b
DABCO	3.3×10^{6a}	0.68^b
TMPD	8.7×10^8	0.15^c
PQ^{2+} ($\mu = 1.32 \times 10^{-2}$ M (NBu_4TfO))	1.1×10^9	$-0.45(2+/+)^d$
4-carbomethoxy-*N*-methylpyridinium ($\mu = 6.83 \times 10^{-3}$ M (NBu_4TfO))	1.0×10^9	-0.93^b
N-methylnicotinamide ($\mu = 6.74 \times 10^{-3}$ M (NBu_4TfO))	6.3×10^8	
nicotinamide	$<1 \times 10^5$	

[a] For $\tau^0/\tau < 2$. [b] From: Mann, C. K.; Barnes, K. K. "Chemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970. [c] Reference 25. [d] Reference 17a.

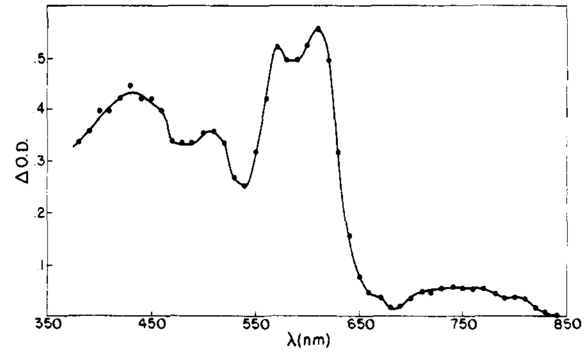

Figure 1. Transient difference spectrum observed 50 μs after conventional flash photolysis ($\lambda_{ex} > 450$ nm) of 7.1×10^{-6} M $Rh_2(br)_4{}^{2+}$ and 7.4×10^{-3} M TMPD in methanol solution (21 °C).

(from the uncorrected emission spectrum) and the λ_{max} of the $^1A_{1g} \rightarrow {}^1A_{2u}$ absorption is 553 nm. The $^1A_{1g} \rightarrow {}^3A_{2u}$ absorption of $Rh_2(br)_4{}^{2+}$ has not been observed, but we expect it to fall between 553 and 800 nm. The triplet energy of $Rh_2(TMB)_4{}^{2+}$ in acetonitrile solution should be somewhat higher, since $\lambda_{max}(^1A_{1g} \rightarrow {}^1A_{2u})$ = 515 nm and the apparent phosphorescence λ_{max} = 770 nm.

Electron Transfer. We have found that both electron donors and electron acceptors react with the $^3A_{2u}$ state of $Rh_2(br)_4{}^{2+}$ (or $Rh_2(TMB)_4{}^{2+}$) to give nonequilibrium products. For oxidative quenching we have studied the methylpyridiniums: PQ^{2+}, *N*-methylnicotinamide, and *N*-methyl-4-carbomethoxypyridinium. The results (Table II) show that the $^3A_{2u}$ state of $Rh_2(br)_4{}^{2+}$ is quenched in all cases except for unsubstituted nicotinamide. From these data we estimate that the upper limit for the reduction potential of $Rh_2(br)_4{}^{3+/2+*}$ in acetonitrile is −0.8 V vs. SCE, since all the pyridiniums quench at near the diffusion-controlled rate.

For reductive quenching we have used the amines TMPD, DABCO, and DMA (Table II). TMPD is quite efficient in deactivating the triplet. DABCO is not so efficient, and quite high concentrations of quencher are required. For DMA, even a 10% solution in acetonitrile does not effect a decrease in emission lifetime of $Rh_2(br)_4{}^{2+*}$ ($^3A_{2u}$). Since the quenching rate drops off for quenchers with potentials between 0.15 and 0.7 vs. SCE, we assume that the reduction potential of $Rh_2(br)_4{}^{2+*/+}$ falls in this range in acetonitrile solution.[24]

Conventional flash photolysis has been used to examine the products of electron-transfer quenching. We have focused on the reactivity of the binuclear rhodium complexes with a single electron donor (TMPD) and a single electron acceptor (PQ^{2+}). For $Rh_2(br)_4{}^{2+}$ in methanol, excitation at wavelengths greater than 450 nm with 5×10^{-3} M TMPD in solution gives the transient difference spectrum shown in Figure 1. The absorption at ~600 nm is due to $TMPD\cdot^+$, whereas the absorptions at ~740 and ~430 nm are attributable to a new $Rh_2(br)_4{}^{n+}$ species. There is no apparent bleaching at any wavelength, and we believe this is due to the combined absorption of $Rh_2(br)_4{}^{n+}$ and $TMPD\cdot^+$ being larger than the absorption loss from $Rh_2(br)_4{}^{2+}$. The back-reaction follows second-order kinetics to give the original ground-state species ($k_b = (1.0 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$ (21 °C)).[25] The rate law suggests that the transient rhodium species is $Rh_2(br)_4{}^+$, the back-reaction being a simple one-electron-transfer process. Further support for this interpretation comes from a nanosecond flash photolysis experiment using 337-nm excitation: a $Rh_2(br)_4{}^{2+}$ solution with $\sim 10^{-1}$ M DABCO in acetonitrile gives partial quenching of the $^3A_{2u}$ emission and transient absorption directly as the emission decays. This absorption is similar to that expected for $Rh_2(br)_4{}^{n+}$, as determined in the TMPD experiment. Thus, it appears that $Rh_2(br)_4{}^{n+}$ is produced directly upon quenching and not by a secondary process. Since TMPD and DABCO are one-electron donors, it follows that $Rh_2(br)_4{}^{2+*}$ ($^3A_{2u}$) is a one-electron acceptor.

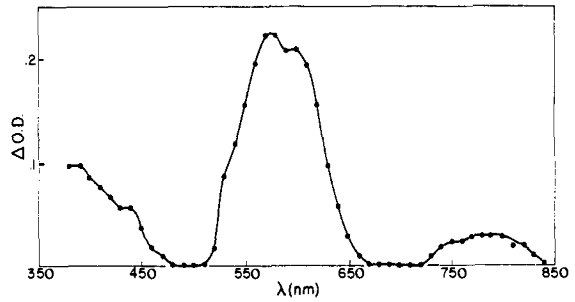

Figure 2. Transient difference spectrum observed 50 μs after conventional flash photolysis ($\lambda_{ex} > 450$ nm) of 7.7×10^{-6} M $Rh_2(TMB)_4{}^{2+}$ and 1.1×10^{-2} M TMPD in methanol solution (21 °C).

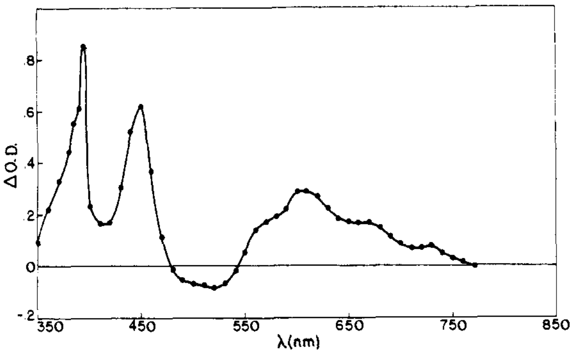

Figure 3. Transient difference spectrum observed 50 μs after conventional flash photolysis ($\lambda_{ex} > 450$ nm) of 7.7×10^{-6} M $Rh_2(TMB)_4{}^{2+}$ and 6.5×10^{-3} M paraquat chloride in methanol solution (21 °C).

Similarly, we have observed the products of the reaction of TMPD with the triplet of $Rh_2(TMB)_4{}^{2+}$ in methanol. The transient spectrum, taken 50 μs after excitation (with $\lambda > 450$ nm), is shown in Figure 2. The spectrum is quite similar to that produced by flash photolysis of $Rh_2(br)_4{}^{2+}$/TMPD in methanol. No bleaching at the ground-state absorption maximum is seen, and this implies that the combined absorption of $Rh_2(TMB)_4{}^{n+}$ and $TMPD^+$ at 515 nm is greater than the absorption loss. Again, the back-reaction follows second-order kinetics ($k_b = (1.6 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$ (21 °C)).[25] Since the spectroscopic and reactivity properties are similar to those of the $Rh_2(br)_4{}^{n+}/TMPD\cdot^+$ pair, a one-electron-reduced species, $Rh_2(TMB)_4{}^+$, is believed to be involved.

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(24) Determination of the reduction potential $Rh_2(br)_4{}^{2+/+}$ has proved difficult, owing to the complex chemical behavior of $Rh_2(br)_4{}^+$. From cyclic voltammetric measurements at rapid sweep rates, we have determined that the potential is about −1.4 V vs. SCE in acetonitrile solution; thus the reduction potential of $Rh_2(br)_4{}^{2+*}$ ($^3A_{2u}$) is estimated to be 0.3 V vs. SCE (Najdzionek, J.; Gray, H. B., unpublished results).

(25) This rate constant is based on ϵ(612 nm) = $1.3 \times 10^4\ M^{-1}\ cm^{-1}$ for $TMPD\cdot^+$ in acetonitrile solution (Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *J. Am. Chem. Soc.* **1977**, *99*, 1980). We assume that the contribution to 612-nm absorption from the rhodium complex is small.

We have also quenched $Rh_2(TMB)_4^{2+*}$ ($^3A_{2u}$) with PQ^{2+} in methanol. Excitation at wavelengths longer than 450 nm produces the transient spectrum shown in Figure 3. The absorption features at wavelengths greater than 600 nm and near 395 nm are attributed mainly to $PQ\cdot^+$.[26] The bleaching near 515 nm and the absorption at 450 nm are from the binuclear rhodium complex. We attribute the 450-nm absorption to the one-electron-oxidized rhodium species, $Rh_2(TMB)_4^{3+}$; the back-reaction between $Rh_2(TMB)_4^{3+}$ and $PQ\cdot^+$ obeys second-order kinetics (k_b = (2.2 ± 0.5) × 10^8 M^{-1} s^{-1} (21 °C) (μ = 1.95 × 10^{-2} M). We have previously shown[5,6] that flash photolysis of $Rh_4(br)_8^{6+}$ in 1 N H_2SO_4 leads to transient production of $Rh_2(br)_4^{3+}$. The difference spectrum in this case is dominated by bleaching of the ground-state absorption and a large absorption peak at 440 nm. The intensity and shape of this absorption band are very similar to those associated with the peak at 450 nm attributed to $Rh_2(TMB)_4^{3+}$, providing further confirmation that the transient comes simply from one-electron oxidation of $Rh_2(TMB)_4^{2+*}$ ($^3A_{2u}$).

Flash photolysis of $Rh_2(br)_4^{2+}/PQ^{2+}$ in acetonitrile solution produced a transient spectrum (50 μs after the flash) that is very similar to that of the $Rh_2(TMB)_4^{2+}/PQ^{2+}$ system in methanol; the absorption maximum of $Rh_2(br)_4^{3+}$ is at 435 nm and bleaching is observed at 550 nm. However, in this system the kinetics are very complex, owing to the fact that $Rh_2(br)_4^{3+}$ can react with itself or with $Rh_2(br)_4^{2+}$ to give $Rh_4(br)_8^{n+}$ (n = 5, 6).[6] These Rh–Rh bond-forming reactions compete with electron back-transfer and thus give secondary products which themselves eventually react with $PQ\cdot^+$ to give $Rh_2(br)_4^{2+}$ and PQ^{2+}. In the case of $Rh_2(TMB)_4^{2+}$, the methyl groups on the ligand inhibit association of the partially oxidized binuclear species,[7] and electron back-transfer predominates.

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[26] For $PQ^{+}\cdot$, ϵ(395 nm) = 2.9 × 10^4 M^{-1} cm^{-1} (Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5224).

Thermochemistry and Dissociation Dynamics of State-Selected C_4H_4X Ions. 1. Thiophene

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Abstract: The threshold photoelectron spectrum of thiophene and photoionization efficiency curves for $C_4H_4S^+$, $C_4H_3S^+$, C_3HS^+, $C_2H_2S^+$, CHS^+, and $C_3H_3^+$ from thiophene were measured in the 8–14-eV photon energy range. $C_2H_2S^+$ is the only fragment produced below 12.9 eV, and its thermochemical dissociation onset was determined to be 12.1 ± 0.1 eV. The dissociation rates of internal energy selected thiophene ions in the 12–12.6-eV photon energy range were determined by photoion–photoelectron coincidence (PIPECO). In addition, the average kinetic energy released in the dissociation to $C_2H_2S^+$ and C_2H_2 was determined in the 13–14-eV photon energy range. The ion lifetimes and kinetic energy release results were compared to predictions of the statistical theory (RRKM/QET). Good agreement between measured and predicted lifetimes was noted when a linear $C_4H_4S^+$ transition state and product $C_2H_2S^+$ ion were assumed. The measured kinetic release is approximately twice that predicted by the quasi-equilibrium theory.

Introduction

The gas-phase chemistry of ions has been an active area of research ever since the advent of mass spectrometry. An important goal has been the elucidation of the dissociation mechanisms of highly excited ions in order to predict the structure of the neutral precursor molecule from the distribution of fragment ions observed in a mass spectrometer.

The study of gas-phase ions is also of interest in its own right and because it makes possible comparisons between the reactions of gas-phase ions and those of ions in solution. Two major differences between these two phases are the stability and deexcitation of ions. In solution, ions are stabilized by solvation and any excited states are rapidly deexcited by collisions. On the other hand, ions in a mass spectrometer are often formed in excited states at low pressures and lose their energy primarily via unimolecular processes such as fluorescence or dissociation. As a result, one of the problems in studying gas-phase ion chemistry in conventional mass spectrometers is the broad and generally unknown distribution of internal energy of the ions.

A major advance in our understanding of ionic dissociations was the application of the statistical theory called the quasi-equilibrium theory (QET)[1] to reactions occurring in the mass spectrometer. At about the same time and independently, Marcus and Rice[2] developed an improved version of the old RRK[3] theory, which is now referred to as the RRKM theory. Although the two theories are identical in their fundamental statistical assumptions, the QET expressed its rate $k(E)$ as a function of the internal energy E while the RRKM theory went beyond this form to the thermalized rate, k(T) which is more appropriate to thermalized neutral systems. In its most basic form, the dissociation rate of a molecule (or ion) with internal energy, E, and an activation energy of E_0 is given by eq 1, where ρ and $\rho^\ddagger$ are the density of

$$k(E) = \sigma \sum_{\epsilon=0}^{E-E_0} \rho^\ddagger(\epsilon)/h\rho(E) \qquad (1)$$

vibrational and internal rotational states of the molecule (or ion) and the transition state, respectively. The parameter σ is a small number which accounts for the number of equivalent ways the molecule can dissociate and h is Planck's constant. The numerator sums over the number of energetically allowed ways of passing through the region of the transition state. This is because $E - E_0$, the energy in excess of that required to pass over the transition state, can be partitioned among the vibrational and internal ro-

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[1] H. M. Rosenstock, M. B. Wallenstein, A. L. Warhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 667 (1952).

[2] R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951).

[3] (a) O. K. Rice and H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927); (b) L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

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