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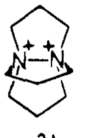
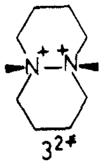
Estimation of Strength of the "Three-Electron σ Bond" of a Hexaalkylhydrazine Monocation Radical

Sir:

One-electron reduction of tricyclic hexaalkylhydrazine dications $\mathbf{1}^{2+}$ [1] and $\mathbf{2}^{2+}$ [2] has been shown to give very long-lived red radical cations which appear to be best described as having "three-electron σ bonds", i.e., with one electron in an orbital which is largely σ* N–N in character. We report here that the less constrained dication $\mathbf{3}^{2+}$ [3] gives a similar but much shorter lived species, whose lifetime allows estimation of the strength of the three electron bond for this molecule.


1^{2+}


2^{2+}


3^{2+}

Solvated electrons were produced by pulse radiolysis[4] of N_2-saturated water containing 0.1 M *tert*-butyl alcohol, to scavenge the hydroxyl radicals produced, and 1–2 × 10^{-4} M dication. Decay of optical absorption of e_{aq}^- was monitored at 600 nm and was accompanied by growth of monocation radical $\mathbf{1}^{+\cdot}$–$\mathbf{3}^{+\cdot}$ absorption. All three dications react rapidly with e_{aq}^- (see Table I), although the rate constant for $\mathbf{1}^{2+}$ reduction is significantly lower than that for the other two. A larger geometry change upon accepting an electron is suggested for system **1** by the 14.7-G nitrogen splitting constant of $\mathbf{1}^{+\cdot}$ (indicating nearly planar nitrogens) than for **2**, because a(N) of $\mathbf{2}^{+\cdot}$ is 34.4 G (indicating nearly tetrahedral nitrogens).[1,2] Interestingly, these dications are not reduced by isopropyl alcohol radical ($\cdot CMe_2OH$, generated by pulse radiolysis of N_2O-saturated water containing 10^{-1} M isopropyl alcohol), despite the fact that the electron transfer is quite exothermic.[5] A substantial steric effect on the rate of electron transfer appears to be involved. All three radical cations have very similar absorption spectra (see Table I). Those observed for $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ agree well with data obtained by conventional methods, although a significantly higher ϵ value was observed for $\mathbf{1}^{+\cdot}$ in this work. We presume that partial decomposition had occurred in the samples of $\mathbf{1}^{+}$ previously prepared.[1]

Although $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ are known to be long lived, the optical absorptions of these species were found to disappear partially in a rapid process. This is indicated by the optical spectra before and after this rapid decay which are identical except for intensity. The decay process essentially followed second-order kinetics. These facts would indicate that the radical cations produced react with another transient produced by the pulse which we suggest to be the $\cdot CH_2CMe_2OH$ radical. This latter species is formed by the reaction of $OH\cdot$ radicals and $H\cdot$ atoms with *tert*-butyl alcohol and in a yield exceeding that of the radical cation only by 20–25%. The only partial decay of the radical cation absorption is explained by the fact that the $\cdot CH_2CMe_2OH$ + $\mathbf{1}^{+\cdot}$ ($\mathbf{2}^{+\cdot}$ or $\mathbf{3}^{+\cdot}$) reaction ($k_2 \sim 2\text{–}3 \times 10^9$ M^{-1} s^{-1}) has to compete with the bimolecular decay of two $\cdot CH_2CMe_2OH$ radicals ($2k_2 = 1.3 \times 10^9$ M^{-1} s^{-1}).

Because $\mathbf{2}^{+\cdot}$ cannot be reacting by addition to the weak three electron σ bond as this would require a nitrogen inversion which is far too costly in energy to be consistent with the rapid

Table I. Rate Constants for Reaction of Hexaalkylhydrazine Dications with e_{aq}^-, and Absorption Maxima of the Products

starting compound	k_2, M^{-1} s^{-1}, for e_{aq}^- + dication	cation radical, λ_{max}, nm (ϵ, M^{-1} cm^{-1})
1^{2+}	1.4×10^{10}	480 (2600)
2^{2+}	5.0×10^{10}	470 (4500)
3^{2+}	4.9×10^{10}	470 (4600)

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reaction observed, an α-hydrogen abstraction is presumed to be occurring in at least this case. As expected, once the *tert*-butyl alcohol radical is consumed, the optical signals for $\mathbf{1}^{+}\cdot$ and $\mathbf{2}^{+}\cdot$ are completely stable for over 10 s (nonflowing conditions, the slowest time scale that could be employed using the pulse radiolysis equipment). In contrast, the $\mathbf{3}^{+}\cdot$ optical signal decreases by a relatively slow first-order process after the initial fast reaction with $\cdot CH_2CMe_2OH$ is completed. The observed rate constant for $\mathbf{3}^{+}\cdot$ disappearance is $135 \pm 15\ s^{-1}$ at 25 °C, pH independent between 2.7 and 5.3 (the lower limit is imposed by the decreased yield of $\mathbf{3}^{+}\cdot$ when the $e_{aq}^{-} + H^{+}$ reaction consumes too great a fraction of the electrons produced, and the upper limit by decomposition of $\mathbf{3}^{2+}$). We suggest that this uncatalyzed first-order decomposition of $\mathbf{3}^{+}\cdot$ is caused by thermal cleavage of the three-electron σ bond. This cleavage allows the nitrogens to move apart until they no longer interact significantly, and the acidic amine radical cation[6] and basic free amino group produced will undergo very rapid, irreversible net proton transfer at the pH employed; cleavage of the $R_3N\cdots NR_3^{+}$ bond should be irreversible. The 5-ms observed half-life corresponds to $\Delta G^{\ddagger}$ of 14.5 kcal/mol using the Erying equation, which we suggest is an experimental measure of the strength of the three-electron σ bond of $\mathbf{3}^{+}\cdot$. The tricyclic radical cations $\mathbf{1}^{+}\cdot$ and $\mathbf{2}^{+}\cdot$ are structurally prevented from cleaving the N–N bond and have solution lifetimes of hours and months, respectively.[1,2]

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(3) *N,N*-Dimethylpiperazine (Snyder, H. R.; Michels, J. G. *J. Org. Chem.* **1963,** *28*, 1144) was heated with excess 1,4-dibromobutane at 100 °C for 15 min. The resulting monoquaternary salt was treated with $AgBF_4$ in aqueous HBF_4 and after filtration with AgBr, **3** $(BF_4)_2$, mp 166–167 °C, was precipitated upon addition of ethyl alcohol. Satisfactory analytical and spectroscopic data were obtained. In particular the ^{13}C NMR in D_2O/D_2SO_4 at 25 °C showed signals at 16.4 (double intensity), 49.7, 61.6, and 65.6 ppm, and the signals at 61.6 and 65.6 coalesced to a single line at 60 °C, showing that the cis isomer had been obtained. An attempt to prepare the trans isomer by double methylation of 1,6-diazabicyclo[4.4.0]decane with $MeOSO_2F$ led to no more than monoalkylation.

(4) The 1.6- and 4.0-MeV van de Graaff generator pulse radiolysis apparatus at the H.M.I. was employed in this work.

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Synthesis of a Class of Complexes Containing Tungsten–Tungsten Quadruple Bonds

Sir:

Despite the large number of complexes of Mo containing quadruple metal–metal bonds, few are known for W.[1] This probably is due largely to the fact that a W analogue of $Mo_2(OAc)_4$ (the major starting material for preparing complexes containing quadruple bonds) has not yet been prepared.[2] We have been attempting to systematize the chemistry of tungsten halides and have found that a class of complexes with the formula $W_2Cl_4L_4$ (L = a phosphine ligand) can be prepared readily, either by reducing $[WCl_4]_x$ with sodium amalgam in the presence of L or by pyrolyzing monomeric W(II) complexes. The former demonstrates that, once a metal–metal bond of order greater than one is present, it will quite likely survive upon reducing the metal to give a bond of higher order.[3]

Phosphines react fairly slowly with WCl_4 suspended in THF to yield WCl_4L_x (x = 2 or 3) complexes. However, when 2 equiv of sodium amalgam (0.4%) is added to a stirred mixture of WCl_4 and PBu_3 in THF at −20 °C and the mixture is warmed to room temperature, WCl_4 is consumed and the solution turns blue-green. $W_2Cl_4(PBu_3)_4$ can be isolated in high yield after filtering the mixture through Celite. Analogous green to blue-green complexes (**1**) containing PMe_3, PMe_2Ph, or $PMePh_2$ can be obtained similarly in 60–80% yield (eq 1). We have also used this method to prepare more simply and directly one member [blue $Mo_2Cl_4(PBu_3)_4$] of the well-known class of analogous molybdenum complexes.[4]

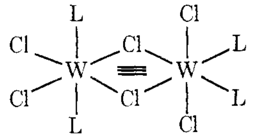
$$WCl_4 + 2Na/Hg + 2L \xrightarrow{THF} W_2Cl_4L_4\ (\mathbf{1}) \qquad (1)$$

$$L = PMe_3,\ PMe_2Ph,\ PMePh_2,\ \text{or}\ PBu_3$$

The reaction fails to give $W_2Cl_4(L\text{-}L)_2$ (**2**, L-L = dmpe or diphos) directly. These must be prepared by displacing PBu_3 from $W_2Cl_4(PBu_3)_4$ in toluene at 80 °C. Sparingly soluble, brown $W_2Cl_4(diphos)_2$ or green $W_2Cl_4(dmpe)_2$ crystallize from the reaction mixture in 60 and 95% yields, respectively. Actually brown $W_2Cl_4(diphos)_2$ contains ~10% green crystalline form. (Two forms of $Mo_2Cl_4(diphos)_2$ were also isolated.[5])

The formulations of **1** and **2** are based on elemental analyses[6] and the following data (cf. the analogous Mo complexes[4,5]). All are air stable in the solid state and only moderately sensitive in solution. A cryoscopic molecular weight determination for $W_2Cl_4(PBu_3)_4$ (calcd 1317; found 1320) and parent peaks in the mass spectra of $W_2Cl_4(PMe_3)_4$ and $W_2Cl_4(dmpe)_2$ show that they are dimers. The ^{31}P and ^{1}H NMR spectra are virtually identical with those reported for the $Mo_2Cl_4L_4$ complexes except for the presence of ^{185}W satellites in the ^{31}P spectra.[7] A Raman spectrum[8] of $W_2Cl_4(PBu_3)_4$ revealed an intense peak at $260 \pm 10\ cm^{-1}$ which we tentatively assign as the tungsten–tungsten stretch.

If only 1 equiv of sodium amalgam is used, a mixture of WCl_4 and PMe_3 yields a red solution from which red, crystalline $W_2Cl_6(PMe_3)_4$ (**3a**) can be isolated in 75% yield. We believe that **3a** has a structure analogous to the known $W_2Cl_6Py_4$ (**3b**)[9] based on the fact that its ^{1}H NMR spectrum shows two types of phosphine ligands. The reduction of **3a** with 1 more equiv of sodium amalgam/W yields $W_2Cl_4(PMe_3)_4$ in 80% yield.



3a, L = PMe_3
b, L = Py
c, L = THF

If phosphine is absent, 1 equiv of sodium amalgam reduces WCl_4 to give a greenish yellow solution in which greenish yellow crystals form on addition of pentane. Since the ^{1}H NMR spectrum of this complex shows two types of THF li-