The Trialkylhydrazyl–Trialkylhydrazine Radical Cation Proton Transfer. 1. Equilibrium Constant

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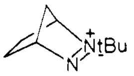
Abstract: Pulse radiolytically generated e_{aq}^- and $\cdot C(CH_3)_2OH$ in water reduce trialkyldiazenium salts ($R_3N_2^+$) to hydrazyl radicals ($R_3N_2\cdot$), which protonate to give hydrazine radical cations ($R_3N_2H^{+}\cdot$). Determination of pK_a($R_3N_2H^{+}\cdot$) by conductivity measurements gave 7.0 (±0.4), 7.0 (±0.4), 8.3 (±0.2), and 10.4 (±0.2) for the radical cations of 2-*tert*-butyl-2,3-diazabicyclo[2.2.1]heptane (**1**H$^{+}\cdot$), its 7-spirocyclopropyl analogue (**2**H$^{+}\cdot$), 2-*tert*-butyl-2,3-diazabicyclo[2.2.2]octane (**3**H$^{+}\cdot$), and 9-*tert*-butylamino-9-azabicyclo[3.3.1]nonane (**4**H$^{+}\cdot$), respectively. The respective values for pK_a($R_3N_2H_2^+$) − pK_a($R_3N_2H^{+}\cdot$) are +2.1, +2.4, +1.2, and −2.6. The hydrazyl radical and hydrazine radical cation have similar absorption spectra except for system **4**, where a significant red shift in UV maximum of the hydrazyl relative to that of the hydrazine radical cation was observed. The deviant behavior of the *N,N*-cycloalkyl compound **4** from the *N,N'*-cycloalkyl compounds **1**–**3** is argued to result from **4**· being more twisted about the NN bond than **4**H$^{+}\cdot$, while such twisting does not occur in the *N,N'*-cycloalkyl systems.

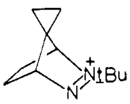
Considerable effort has been put into mechanistic understanding of the early steps in hydrazine oxidations,[2a] the first three steps of which for reaction of a trialkylhydrazine with a one-electron oxidant are shown in Scheme I. The thermodynamics of the two-electron transfers are reasonably well understood through study of structure–reactivity effects on the formal redox potential $E^{\circ\prime}$ of tetraalkylhydrazine oxidation (R_4N_2, $R_4N_2^{+}\cdot$)[2b,c] and trialkyldiazenium salt reduction ($R_3N_2\cdot$, $R_3N_2^+$).[3] Both three-electron π-bonded species $R_4N_2^{+}\cdot$[4] and $R_3N_2\cdot$[3] are preferentially sp^2 hybridized at nitrogen. Little is known about the intermediate proton transfer step in Scheme I. Although hydrazine radical cations with NH bonds have been observed by ESR in flow systems using acidic solvents,[5] they are not long lived in the presence of bases, nor are hydrazyl radicals long lived in protic solvents, so study by most methods is not fruitful.

The pK_a values of $H_4N_2^{+}\cdot$ and $Me_2H_2N_2^{+}\cdot$ with respect to deprotonation were reported to be 7.10 ± 0.1 and 7.9 ± 0.2, respectively,[6] determined from the optical absorptions of these species measured after the reaction of the hydrazines with pulse radiolytically generated OH· radicals at various pH values.

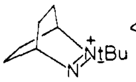
The present study has been concerned with the proton-transfer equilibrium of Scheme I for bicyclic trialkylhydrazines. The hydrazyls were generated by one-electron reduction of trialkyldiazenium salts **1**$^+$–**4**$^+$, using pulse-radiolysis techniques. It is necessary that no $C_\alpha H$ bonds which can have significant overlap with a p orbital at either nitrogen be present, or rapid decomposition of the diazenium salt to the more stable amino immonium salt occurs in protic solvents.[8] The Bredt's rule effect of holding the $C_\alpha H$ bonds in the nodal plane of the nitrogen p orbitals makes such decomposition unfavorable, and **1**$^+$–**4**$^+$ are stable in water between pH 2 and 13. The hydrazyls derived by one-electron reduction have extremely long half-lives in nonprotic solvents (hours to weeks[3]), so the very rapid hydrogen transfer disproportionation reactions undergone by unprotected alkylhydrazyls[9] will not interfere with studying the protonation reaction.



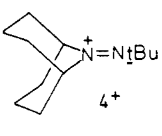
1$^+$



2$^+$

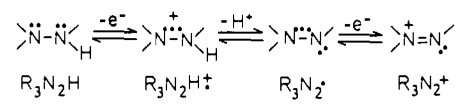


3$^+$



4$^+$

Scheme I



Results

Choice of Reductants. Pulse-radiolysis studies were carried out on 10^{-4} M $R_3N_2^+$ salts in water. Because water is present in huge excess, the primary process is the well-established generation of the water fragments shown in the equation

$$H_2O \rightarrow e_{aq}^- + H_{aq}^+ + OH\cdot + H\cdot + H_2 + H_2O_2 \qquad (1)$$

To observe $R_3N_2\cdot$ formed in the reaction

$$e_{aq}^- + R_3N_2^+ \rightarrow R_3N_2\cdot \qquad (2)$$

without the complication of producing other species, particularly by the highly reactive hydroxyl radical, the latter had to be removed by addition of suitable scavengers. In initial studies, we employed the common technique of adding 0.1 M *tert*-butyl alcohol to the solution, to scavenge ·OH by eq 3, which has a second-order rate constant of 5.2×10^8 M^{-1} s^{-1} [10] and produces principally the redox-inactive $\cdot CH_2CMe_2OH$ radical. The 1000-fold excess of alcohol over diazenium salt causes hydroxyl

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(1) (a) University of Wisconsin. (b) Hahn-Meitner-Institut für Kernforschung.

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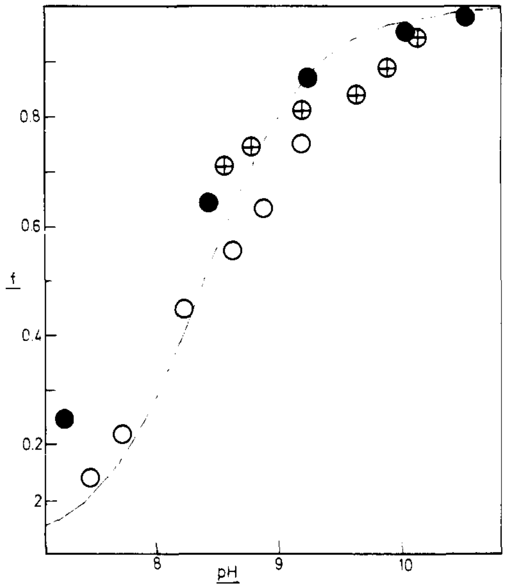


Figure 1. Plot of fraction of **3·** vs. pH, from conductivity data: filled circles, *tert*-butyl alcohol/N_2 system; open circles, 2-propanol/N_2O system; crossed circles, HCO_2^-/N_2O system. The line is theoretical for $pK_a = 8.3$.

radical to react virtually exclusively by eq 3. From the other primary species listed in eq 1 only the H· atom might also have a high enough reactivity to interact directly with $R_3N_2^+$ on the time scale of interest. (The rate constant for the reaction of H· with *tert*-butyl alcohol is only about 10^5 M^{-1} s^{-1}.) Its yield, however, is relatively small, and by comparison with the results from solutions containing formate or 2-propanol instead of *tert*-butyl alcohol a possible reaction of H· with $R_3N_2^+$ does not noticeably interfere.

$$\cdot OH + CH_3CMe_2OH \rightarrow H_2O + \cdot CH_2CMe_2OH \qquad (3)$$

The rate constant for eq 2 was measured to be 3.9×10^{10} M^{-1} s^{-1} for **1**$^+$ by observing the disappearance of e_{aq}^- absorption at 600 nm. Reductions of **2**$^+$–**4**$^+$ are also close to diffusion controlled, although accurate rate measurements were not made.

The hydrazyl formed in eq 2 shows optical absorption in the UV. Optical measurements made at various pH revealed only slight differences between the spectra of $R_3N_2\cdot$ and the protonated form $R_3N_2H^{+}\cdot$. To establish the associated equilibrium constant it was therefore more appropriate to employ conductivity techniques. The relevant processes are given in eq 1, 2, and 4–6.

$$H^+ + OH^- \rightarrow H_2O \qquad (4)$$

$$R_3N_2\cdot + H_2O \rightleftarrows R_3N_2H^{+}\cdot + OH^- \text{ (in base)} \qquad (5)$$

$$R_3N_2\cdot + H^+ \rightleftarrows R_3N_2H^{+}\cdot \text{ (in acid)} \qquad (6)$$

In base the proton produced in the radiolysis of water (eq 1) is rapidly neutralized by eq 4 ($k_4 = 1.4 \times 10^{11}$ M^{-1} s^{-1}). In strong enough base so that $R_3N_2\cdot$ is completely unprotonated, the conductivity change will be given by summing eq 1–4: $\Delta\Lambda = -\Lambda(OH^-) - \Lambda(R_3N_2^+) = -180 - \text{ca. } 40 \simeq -220\ \Omega^{-1}\ cm^2$. Taking equilibrium 5 into account and considering that the specific conductivities of organic cations are rather similar (about 30–40), one expects to see $\Delta\Lambda \simeq -220f$, where f is the fraction of unprotonated hydrazyl: $f = [R_3N_2\cdot]/([R_3N_2\cdot] + [R_3N_2H^{+}\cdot])$. When hydrazyl protonation occurs in acid solutions, then the net result of eq 1–3 and 6 is effectively replacement of $R_3N_2^+$ by $R_3N_2H^{+}\cdot$, i.e., $\Delta\Lambda \simeq 0$. Where $R_3N_2\cdot$ is the predominant species in acid, $\Delta\Lambda = \Lambda(H_{aq}^+) - \Lambda(R_3N_2^+) \simeq 315 - 40 \simeq 275$, and generally an increase of $\Delta\Lambda = 275f$ with $0 \leq f \leq 1$ would describe eq 6. The experimental data are shown in Figures 1 and 2 for the radicals from **3**$^+$ and **4**$^+$, respectively (open circles). The pK_a values for the radical protonation equilibria derived from these and corresponding experiments with **1**$^+$ and **2**$^+$ are listed in Table I.

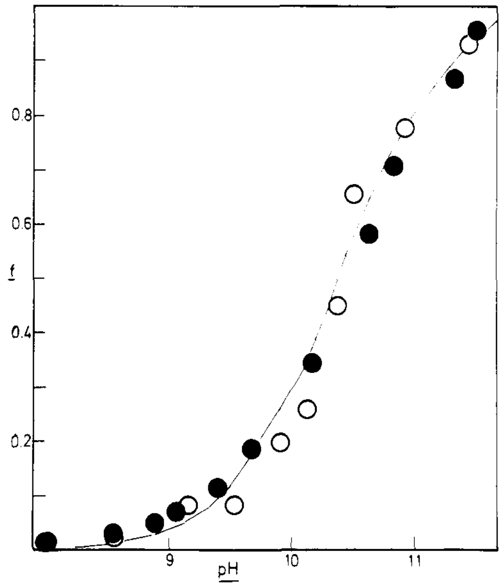


Figure 2. Plot of fraction of **4·** vs. pH, from conductivity data: open circle, *tert*-butyl alcohol/N_2 system; filled circle, 2-propanol/N_2O system. The line is theoretical for $pK_a = 10.4$.

Table I. Acidity Constants and Optical Spectra of Some Trialkylhydrazine Radical Cations

diazenium salt ($R_3N_2^+$)	pK_a-($R_3NH^{+}\cdot$)	λ_m (ϵ) $R_3N_2H^{+}\cdot$	λ_m (ϵ) $R_3N_2\cdot$
1^+	7.0 ± 0.4	285 (1.1×10^3)	270 (1.5×10^3)
2^+	7.0 ± 0.4	290 (1.2×10^3)	275 (1.7×10^3)
3^+	8.3 ± 0.2	260 (2.0×10^3)	260 (2.3×10^3)
4^+	10.4 ± 0.2	290 (3.3×10^3)	270 (3.5×10^3)

An interesting observation was that, although **1·** to **4·** are known to be stable for hours in nonprotic solvents, the conductivity signal in base decreased in magnitude on a time scale of milliseconds in the experiment described. A reaction worth considering would be the electron transfer disproportionation shown as eq 7

$$R_3N_2\cdot + R_3N_2H^{+}\cdot \rightarrow R_3N_2^+ + R_3N_2H \qquad (7)$$

$$R_3N_2H + H_2O \rightleftarrows R_3N_2H_2^+ + OH^- \qquad (8)$$

since $E°'(R_3N_2\cdot, R_3N_2^+)$ is -0.7 V vs. SCE for **1**, and is probably 0.9 V negative of $E°(R_3N_2H, R_3N_2H^{+}\cdot)$, making eq 7 some 20 kcal/mol exothermic. Although reaction 7 does not directly affect $\Delta\Lambda$ since it merely replaces one organic cation by another, it does generate a new proton-transfer equilibrium with a different pK_a, which will affect $\Delta\Lambda$. Reaction 7 is expected to have a maximum rate at $pK_a(R_3N_2H^{+}\cdot)$. The observed rate of conductivity signal disappearance does not, however, drop off properly at high pH for eq 7 and 8 to explain the instability of the conductivity signals. A more satisfactory explanation for the observed decay of the conductivity signal and of the corresponding optical absorption is the radical–radical reaction

$$R_3N_2\cdot + \cdot CH_2CMe_2OH \rightarrow R_3N_2CH_2CMe_2OH \qquad (9)$$

possibly yielding a tetraalkylhydrazine. The yield of both radicals is almost the same with $G(R_3N_2\cdot) = G(e_{aq}^-) \approx G(\cdot CH_2CMe_2OH) = G(\cdot OH) = 2.8–3.0$ species/100 eV absorbed energy. In accordance with this consideration the decay of the signals is of second order and a bimolecular rate constant $k_9 \simeq 6 \times 10^8$ M^{-1} s^{-1} (for **3·**) is derived. It was shown that $\cdot CH_2CMe_2OH$ does not react rapidly enough with $R_3N_2^+$ to compete with its own self-destruction by irradiating N_2O-saturated 0.1 M *tert*-butyl alcohol solutions (in which e_{aq}^- is converted to OH· by N_2O, see eq 10). Only the weak, transient $\cdot CH_2CMe_2OH$ optical spectrum[10] was observed, and none attributable to hydrazine cation radicals or hydrazyls. Because the rapid $\cdot CH_2CMe_2OH–R_3N_2\cdot$ reaction (eq 9) complicates the decomposition kinetics, introduces new species,

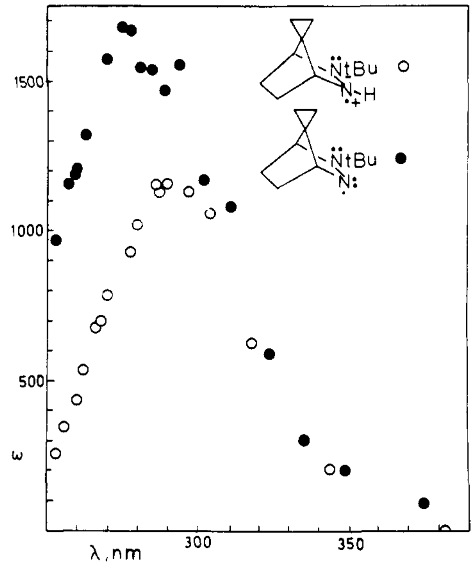


Figure 3. Comparison of the absorption spectra of $2H^{+}\cdot$ (open circles) and $2\cdot$ (filled circles).

and disturbs the optical measurements because $\cdot CH_2CMe_2OH$ absorbs (weakly) where $R_3N_2\cdot/R_3N_2H^{+}\cdot$ absorb, other scavenging systems for generating hydrazyl radicals were also investigated.

Some experiments were run with 3^+ employing N_2O-saturated 0.01 M sodium formate. In such solutions the primary reactive species e_{aq}^-, $\cdot OH$, and $H\cdot$ are all converted by the equations

$$e_{aq}^- + N_2O + H_2O \rightarrow \cdot OH + OH^- + N_2 \qquad (10)$$

$$H\cdot(HO\cdot) + HCO_2^- \rightarrow CO_2^-\cdot + H_2(H_2O) \qquad (11)$$

into $CO_2^-\cdot$, a species that has reducing properties and reacts with the hydrazenium via the equation

$$CO_2^-\cdot + 3^+ \rightarrow 3\cdot + CO_2 \qquad (12)$$

The yield of this reaction is taken as $G = 6.2$. Considering all relevant equations (1, 10–12) and using $\Lambda(HCO_2^-) = 47$, then $\Delta\Lambda \simeq 133–220f$ in base. This system is, however, also limited since buffering effects lower the sensitivity of the conductivity detection near the pK_a of formic acid.

The most suitable system is an N_2O-saturated solution containing 2-propanol (usually 10^{-1} M) where hydrazyls result from the equations

$$\cdot OH/H\cdot + HCMe_2OH \rightarrow \cdot CMe_2OH + H_2O/H_2 \qquad (13)$$

$$\cdot CMe_2OH + R_3N_2^+ \rightarrow R_3N_2\cdot + H^+ + Me_2CO \qquad (14)$$

The yield of hydrazyl formation is somewhat lower than in the formate system since the reducing $\cdot CMe_2OH$ radicals are formed with only about 85% efficiency in the reaction of $\cdot OH/H\cdot$ with 2-propanol;[11] G(hydrazyl) is 5.6. The conductivity parameters for the 2-propanol system are the same as for the *tert*-butyl alcohol/N_2 solutions, i.e., $\Delta\Lambda = -220f$ and $+275f$ in base and acid, respectively.

The rates for the electron-transfer reactions from $CO_2^-\cdot$ and $\cdot CMe_2OH$ were lower than for the reduction of diazenium ion by e_{aq}^- but still high enough to ensure quantitative reaction. For example, $k_{12} \approx 5 \times 10^8$ M^{-1} s^{-1} and $k_{14} \approx 3 \times 10^8$ M^{-1} s^{-1} for the respective reductions of 3^+.

$R_3N_2H^{+}\cdot/R_3N_2\cdot$ Ratios. The initial conductivity data for 3^+, i.e., those obtained before secondary reactions as in eq 9 could take place, gave reasonable agreement for all three reducing systems studied, as seen in Figure 1. Data for 1, 2, and 4 were only taken using *tert*-butyl alcohol/N_2 and 2-propanol/N_2O systems, and again good agreement between the reducing systems was observed. Figure 2 shows the $\Delta\Lambda$ vs. pH curve generated for 4^+. All pK_a values determined are summarized in Table I.

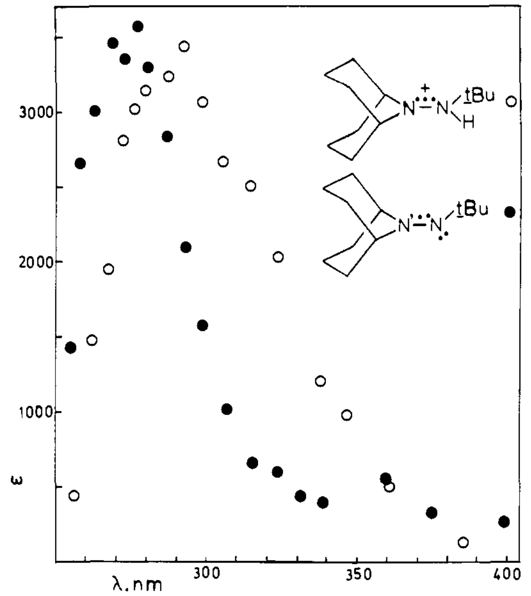


Figure 4. Comparison of the absorption spectra of $4H^{+}\cdot$ (open circles) and $4\cdot$ (filled circles).

Table II. Acidity Constants for Some Protonated Hydrazines (H_2O, 24 ± 1 °C)

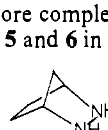
protonated hydrazine	pK_a	protonated hydrazine	pK_a
$1H_2^+$	9.14	$4H_2^+$	7.8[a]
$2H_2^+$	9.37	$5H^+$	7.93
$3H_2^+$	9.51	$6H^+$	8.23

[a] Solubility problems in water. Measured 7.89 in 25% acetone, 7.37 in 50% acetone.

Optical Absorption Spectra. The optical spectra were run at pH values where $R_3N_2H^{+}\cdot$ or $R_3N_2\cdot$ predominate, and the respective λ_{max} and ϵ values are also listed in Table I. Only small differences are found between the unprotonated and protonated forms with the latter showing somewhat higher ϵ values on the high-energy side of the spectrum and probably a slight shift in λ_{max} to shorter wavelengths. On the low-energy side the respective $R_3N_2\cdot$ and $R_3N_2H^{+}\cdot$ spectra practically overlap. A typical example is given in Figure 3, which compares the spectra of $2\cdot$ and $2H^{+}\cdot$. In contrast, the *N,N'*-cycloalkyl system 4 shows a significant displacement of its absorption curves so that ϵ of $4H^{+}\cdot$ is greater than that of $4\cdot$ above about 280 nm, but lower below 280 nm (Figure 4).

Discussion

Acidities of Protonated Hydrazines. Condon[12] has reported pK_a values in water for all 20 H-, methyl-, and ethyl-substituted protonated hydrazines. They range from 7.95 for $H_2NNH_3^+$ to 6.10 for $Me_2NNMe_2H^+$, with a decrease for each NH → NMe substitution, but usually an increase for each NMe → NEt substitution ($pK_a(Et_2NNEt_2H^+)$ is 7.31). Except for some data in dimethyl sulfoxide,[13] little has been published on pK_a values for hydrazines with more complex alkyl groups. We measured the pK_a for protonated 5 and 6 in this work, and also studied 1H–4H



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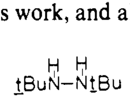

$$t\text{BuNH}-\text{NH}t\text{Bu}$$

6

(see Table II). Although we had solubility problems for 4H, four titrations of the limited amount we could dissolve in water give

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Scheme II

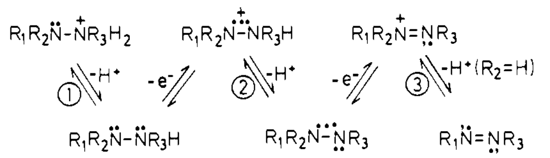


Table III. Acidity Constants for Radical Cations and Protonated Forms of Various Amines

amine (A)	$pK_a(A^{+}\cdot)$	$pK_a(AH^{+})$	ΔpK_a[a]
Me_2NH	7.0 ± 0.5[b]	10.7	+3.7
NH_3	6.7 ± 0.2[b]	9.2	+2.5
$HONH_2$	4.2 ± 0.1[c]	6.1	+1.9
CH_3ONH_2	2.9 ± 0.2[c]	4.6	+1.7
H_2NNH_2	7.1 ± 0.1[d]	8.1	+1.0
$MeNHNH_2$	7.9 ± 0.2[d]	7.2	−0.7
$PhNH_2$	7.0[e]	4.6	−3.9

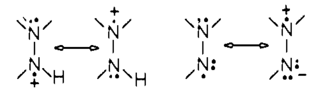
[a] $pK_a(AH^{+}) - pK_a(A^{+}\cdot)$. [b] Reference 17. [c] Reference 18. [d] Reference 6. [e] Reference 19.

7.82 ± 0.03, and we found 7.37 in 50% v/v acetone/water. Substitution of NH by N-*t*-Bu appears to raise pK_a, as indicated by **1**H being 1.2 p*K* units more basic than **5**, and **6** being 0.3 p*K* unit more basic than hydrazine. Increasing branching in an alkyl group also appears to raise pK_a; **6** is 0.7 p*K* unit more basic than the 1,2-dimethyl and 1,2-diethyl compounds.[12]

Acidities of Hydrazine Oxidation Intermediates. It is useful to consider the pK_a values of the species to the right and left of the hydrazine radical cation (equilibrium 2) in Scheme II, where the upper, protonated form to the right differs by loss of a proton and electron from that to the left. Hydrazines are much more basic than azo compounds. Azo compounds are such feeble bases that simple aqueous titrations cannot be employed to measure pK_a for the protonated form, which must be estimated indirectly. The only values determined of which we are aware are −2.93 for protonated azobenzene[14] and −0.05 for protonated di-*tert*-butyldiimide.[15] For the latter case, the hydrazine (**6**) is 8.3 p*K* units more basic than the azo compound of the same substitution. Aqueous titration of 2,3-diazabicyclo[2.2.1]hept-2-ene (the azo analogue of **5**) showed that it is also too feeble a base for such a titration to yield pK_a, so the presence of a cis instead of a trans azo linkage did not cause a large decrease in the hydrazine–azo compound basicity difference in this case.

A large decrease in basicity in going from the approximately sp^3-hybridized hydrazine nitrogen lone pairs to the sp^2-hybridized azo compound lone pairs is well precedented. To quote a literature example for a case with nonadjacent nitrogens, protonated piperazine (sp^3 lone pairs) has $pK_a = 9.86$,[16a] so piperazine is 9.2 p*K* units more basic than its unsaturated analogue pyrazine (sp^2 lone pairs), $pK_a = 0.65$.[16b]

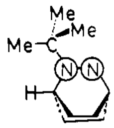
Although the lone pair of a hydrazyl is sp^2 hybridized (because the odd electron MO of a hydrazyl has nearly pure p character, as indicated by ESR splittings[3]), only small $\Delta pK_a = pK_a(R_3N_2H_2^{+}) - pK_a(R_3N_2H^{+}\cdot)$ values are observed for **1**–**3** (2.1, 2.4, and 1.2 p*K* units, respectively), and ΔpK_a for **4** is −2.6 p*K* units, so **4**H is actually less basic than **4**·. Therefore, other factors are clearly opposing the hybridization effect. Analogous pK_a changes from the literature for other substituted amines (A), $\Delta pK_a = pK_a(AH^{+}) - pK_a(A^{+}\cdot)$, appear in Table III. The rather large negative ΔpK_a of aniline seems best interpreted on the basis of resonance stabilization effects. Resonance energy is clearly lost upon protonation of aniline to give $PhNH_3^{+}$, with the positive charge localized on nitrogen, but resonance energy is probably gained upon protonation of phenylamino radical to give $PhNH_2^{+}\cdot$, because charge delocalization into the phenyl ring occurs. There is a decrease in ΔpK_a which overwhelms the hybridization effect, and even results in a negative ΔpK_a value. The ΔpK_a order observed for YNH_2 as Y is changed is $CH_3 > HO > CH_3O > H_2N > CH_3NH$, which is qualitatively the order expected for resonance stabilization in the radical cation. Interaction of a lone pair on Y with the N lone pair is actually slightly destabilizing, as indicated by the gauche conformations adopted by unconstrained hydrazines. Protonation of YNH_2 does not produce a very low-lying empty orbital for stabilization by electron donation from Y. In contrast, protonation of YNH· will cause an increase in stabilization by Y. In resonance-form language, resonance energy will be a maximum when the forms with odd electron on the Y group and the nitrogen are comparable in energy as they are in Ia and Ib (Y = NR_2 is shown), but in contrast, for neutral



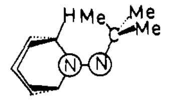
IA IB IIA IIB

YNH·, the form with odd electron present on Y, IIb, must have charge separation and be a less important contributor than IIa. There will be a gain in resonance energy upon protonation of hydrazyl, which we suggest is principally responsible for the low ΔpK_a values of **1**–**3** and the ΔpK_a decrease as more electron-donating Y groups are attached to NH_2.

The ΔpK_a value of **4** is −2.6, indicating an even larger difference in resonance energy for **4**$H^{+}\cdot$ and **4**· than for the other bicyclic systems **1**–**3**. We suggest that such a difference between **1**–**3** and **4** is corroborated by the spectral data of Table I and Figures 3 and 4. In contrast to *N,N′*-bicycloalkyl-*tert*-butylhydrazine systems **1**–**3**, where the hydrazyl and protonated hydrazyl absorption spectra are similar, **4**$H^{+}\cdot$ absorption is markedly red shifted compared with that of **4**·. We suggest that this is caused by a significant geometry difference for these compounds, the degree of twisting about the NN bond in **4**$H^{+}\cdot$ and **4**·, which is not as prevalent for systems **1**–**3**, where the bicyclic ring opposes such twisting. For **4** not only does the *N,N*-bicycloalkyl-*N′*-*tert*-butyl structure not oppose some twisting, but *tert*-butyl bridgehead CH interaction is made more severe, as indicated below.



3·



4·

We propose, then, that **4**· is significantly more twisted[20] than **4**$H^{+}\cdot$, which has a greater resistance to twist because of its higher resonance energy, and this geometry difference leads to the absorption spectrum difference observed for these species. If **4**· really is more twisted, it will have less resonance energy than the untwisted **1**· to **3**·, and, because of a greater resonance-energy difference, a more negative ΔpK_a.

Conclusion

The trialkylhydrazine radical cations studied are either only slightly more acidic than the related protonated hydrazine (1.2–2.4 p*K* units for **1**–**3**) or actually less acidic in one case in which the hydrazyl was argued to be twisted (**4**). The higher resonance energy expected for a hydrazine radical cation than for a neutral hydrazyl radical was argued to be responsible for this result.

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(20) The nitrogen splittings in the ESR of **4**· (11.3, 2 N)[21] are not very different from those of **1**· to **3**· (10.3, 11.0; 10.5 (2 N); 10.6, 11.4, respectively[3]), but calculations[22] indicate that *a*(N) is sensitive both to NN twist (decrease in *a*(N) as twist) and bending at nitrogen (increase as bending increases s hybridization in the spin-bearing orbital), so that a considerable degree of twist and rehybridization could presumably be consistent with the nitrogen splitting observed for **4**·.

Experimental Section

The diazenium salts 1^+–3^+ BF_4^-[3] and 4^+ $CF_3CO_2^-$[21] were prepared by published methods, as were hydrazines 1H–3H.[3]

1,1-(1,5-Cyclooctyl)-2-*tert*-butylhydrazine (4H). A mixture of 4^+-$CF_3CO_2^-$ (0.4 g), sodium borohydride (0.6 g, large excess), and 50 mL of 25% aqueous NaOH was stirred for 12 h at 25 °C and extracted with ether, and the organic layer was dried with calcium chloride and magnesium sulfate and concentrated, giving **4H** as a solid which was purified by VPC.

The pulse-radiolysis equipment (1.55-MeV Van de Graaff generator at the Hahn-Meitner-Institut Berlin) with optical detection of intermediates and the 10-MHz ac conductivity technique have been described.[23] The electron pulse width could be varied; a 1-μs pulse was usually applied. The dose per pulse was typically 300 rad, corresponding to ca. 2×10^{-6} M of primary reacting radicals. Solutions were prepared according to the usual radiation chemical standards. Oxygen was removed from the solutions by bubbling with N_2. All measurements were carried out at room temperature (20–25 °C). The data obtained were digitized by a Biomation 8100 transient recorder and analyzed on line with a PDP-11 computer.

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Selective Dimerization of Monosubstituted α-Olefins by Tantalacyclopentane Catalysts

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Abstract: β,β′-Disubstituted and α,β′-disubstituted tantalacyclopentane complexes (e.g., $Cp''Cl_2\overline{TaCH_2CHMeCHMeCH_2}$; $Cp'' = \eta^5\text{-}C_5Me_5$) are the active intermediates in the catalytic dimerization of $RCH{=}CH_2$ (R = H, Me, *n*-Pr, *n*-Hex, CH_2CHMe_2, CH_2CMe_3) to a mixture of tail-to-tail (tt) dimer (98% when R = Me) and head-to-tail (ht) dimer (100% when R = CH_2CMe_3), respectively, at rates on the order of one turnover/h at 30 °C. The corresponding $\eta^5\text{-}C_5H_5$ catalyst is not indefinitely active, probably because $Ta(\eta^5\text{-}C_5H_5)(olefin)Cl_2$ intermediates are unstable. Deuterium-labeling studies show that each tantalacyclopentane ring contracts to a tantalacyclobutane ring which then rearranges selectively to the tt or ht dimer. We propose that an alkenyl hydride complex is an intermediate in each pathway, that it forms reversibly from the tantalacyclopentane complex, that the rate of the ring contraction step may be kinetically important, and that decomposition of the tantalacyclobutane complex is fast relative to the rate at which it re-forms its alkenyl hydride precursor.

Introduction

For several years metallacyclopentane complexes[2] have been observed as intermediates in catalytic reactions in which a high-energy olefin is cyclodimerized to a cyclobutane derivative.[3] Until recently,[4] however, similar reactions of ordinary olefins had not been observed, at least partly because metallacyclopentane complexes made from them are probably not as favorable thermodynamically. In the meantime, there seemed to be no compelling reason to invoke metallacycles in olefin dimerization reactions.[5]

During our initial investigation of the reactions of ordinary olefins with $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ we discovered that tantalacyclopentane complexes were the ultimate products.[6] Similar $\eta^5\text{-}C_5Me_5$ tantalacycles subsequently were prepared more directly from olefin complexes of the type $Ta(\eta^5\text{-}C_5Me_5)(olefin)Cl_2$.[7] Both are active catalysts for dimerizing α-olefins[8] (e.g., propylene to 2,3-dimethyl-1-butene), although we now find that only the $\eta^5\text{-}C_5Me_5$ type is stable. To our knowledge, this is the only documented example of the use of metallacyclopentane complexes as catalysts for selectively dimerizing α-olefins[9] and the only way to obtain selectively dimers of α-olefins larger than propylene by any route.[10]

Results

Dimerization of $RCH{=}CH_2$ (R = H, Me, Pr, $(CH_2)_5Me$, CH_2CHMe_2, or CH_2CMe_3). The propylene complex, TaCp″-

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(1) (a) NSF Predoctoral Fellow, 1975–1978. (b) ITP Postdoctoral Fellow (Spain), 1977–1981. (c) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978.

(2) In this context we mean only MC_4 complexes, and only those in which the substituents, if any, are alkyl or aryl groups.

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(9) Grubbs recently has suggested[4] that the same Ni metallacycles which give rise to cyclobutane products catalytically also yield the olefin dimers.

(10) (a) The dimerization of propylene has been studied extensively (see ref 5b, p 128, and references cited therein). A product containing essentially only 2,3-dimethylbutenes can be formed by using some Ni catalysts but it is apparently largely 2,3-dimethyl-2-butene. Very recently, a Ni catalyst which gives only 2,3-dimethyl-1-butene (at low temperatures) at a high rate has been developed.[10b] All of these catalysts are postulated to give dimers via olefin insertions into Ni–H and Ni–C bonds. (b) Wilke, G., private communication.

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