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MECHANISTIC STUDIES ON AZOALKANE CATION RADICAL DECOMPOSITION

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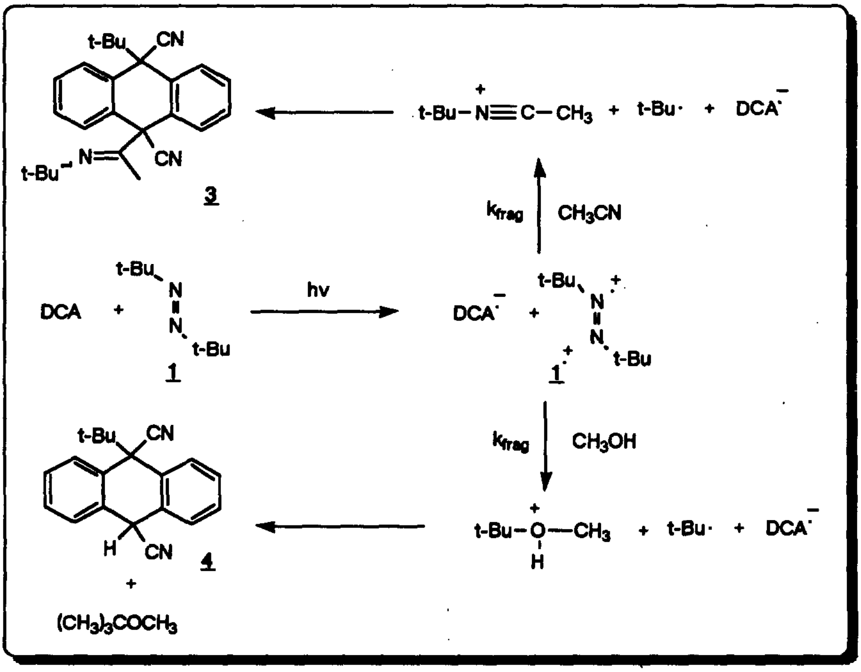
Summary: *We report on the oxidative decomposition of two azoalkanes, azo-bis-2-methyl-2-propane and 3,3,6,6-tetramethyl-1,2-diazacyclohex-2-ene. These azoalkane cation radicals decompose at rates $\geq 10^{18}$ times faster than their neutral precursors. This can be attributed to a decrease of ≥ 24 kcal/mol in the C-N bond dissociation energy on oxidation.*

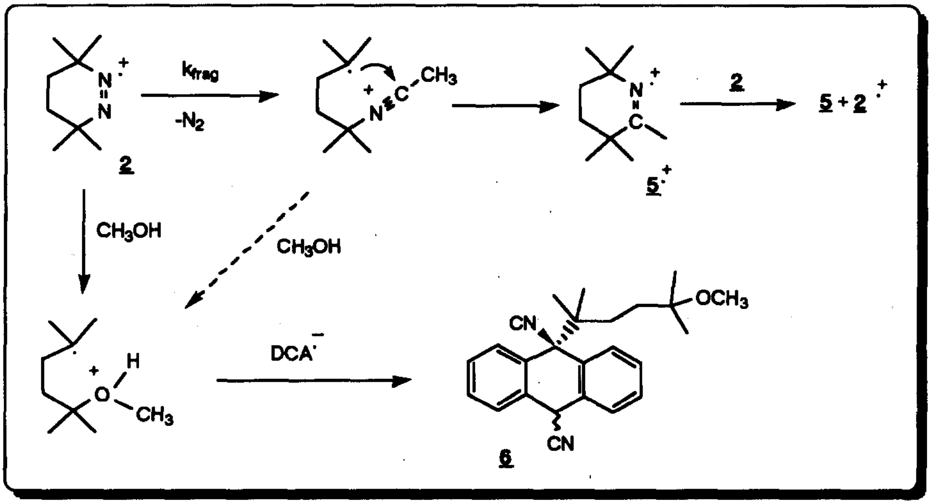
Reactions of organic substrates are often greatly accelerated by one electron oxidation.[1] The oxidation of azoalkanes can result in rapid, highly efficient deazatization.[2] Herein, we report chemical, kinetic and mechanistic studies on the oxidative decomposition of two azoalkanes, azo-bis-2-methyl-2-propane (1),[2f] and 3,3,6,6-tetramethyl-1,2-diazacyclohex-2-ene (2).

Cosensitized photooxidation (> 420 nm) of 1 (0.01 M) using 9,10-dicyanoanthracene (DCA, ca. 10^{-5}) and biphenyl (BP, 0.2 M) in degassed CH_3CN afforded adduct 3 (90%).[3] However, upon the addition of CH_3OH (20% v:v), t-butylmethyl ether (50%) and adduct 4 (80%) are formed.[3] A plausible mechanism for the formation of these products is shown below.[4]



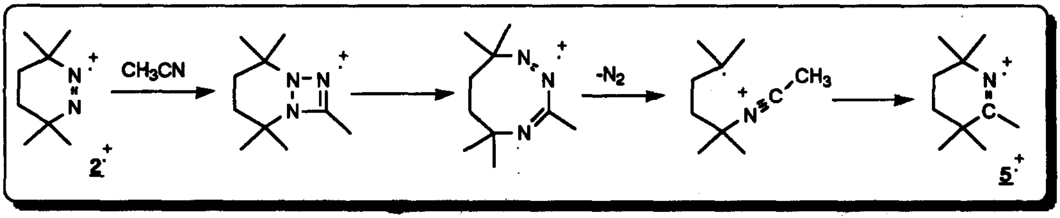
The photogenerated azoalkane cation radical $1^{+\cdot}$ undergoes bond fragmentation with loss of nitrogen producing the t-butyl radical and the nitrilium ion. Coupling of the DCA anion radical, t-butyl radical and the nitrilium ion yields adduct 3. In the presence of CH_3OH, the protonated t-butylmethyl ether is formed in competition or reaction with the nitrilium ion. Coupling of the DCA anion radical with the t-butyl radical followed by protonation affords the adduct 4.

In contrast to 1, cosensitized photooxidation of 2 in CH_3CN afforded the cyclic imine 5 in high yield (75%).[3] The yield of 5 is independent of oxygen concentration ($[O_2] \leq 10^{-3}$ M) and the quantum yield for disappearance of 1 is > 2.[5] However, in the presence of CH_3OH (15% v:v), photoxidation of 2 yields the DCA adduct 6 (90%) instead of the imine.[3] These experimental observations can be rationalized by the following mechanism,



Fragmentation of $2^{+\cdot}$ in CH_3CN yields a nitrilium ion radical intermediate. Intramolecular radical cyclization gives the cation radical $5^{+\cdot}$ which can then oxidize neutral 2. This chain mechanism is supported by the observed quantum yield, and the oxidation potentials of 2 and 5.[6] This radical cyclization must occur rapidly to effectively compete with the reaction of O_2 with the radical center. In the presence of CH_3OH, the protonated ether cation radical intermediate is formed in competition with or from a reaction with the nitrilium cation radical intermediate. Coupling with $DCA^{-\cdot}$ affords the adduct 6.

A plausible alternative mechanism for the formation of products 5 and 6 from the oxidation of 2 (and 3 and 4 from 1), is shown below. Cycloaddition between $2^{+\cdot}$ and CH_3CN followed by electrocyclic ring opening and loss of molecular nitrogen yields the same nitrilium ion radical intermediate as shown above.



However, mass spectral analysis of product 5 obtained from the oxidation of 2 in $CH_3C^{15}N$, showed complete incorporation of the isotopic label. Consequently, this mechanism is not operative in the formation of 5, and presumably 3, 4 and 5, in that it requires no incorporation of the label in product 5.

In order to examine the kinetic behavior of the azo cation radicals $1^{+\cdot}$ and $2^{+\cdot}$, nanosecond absorption spectroscopy (NAS) and photoacoustic calorimetry (PAC) experiments were conducted. Excitation (410 nm, 15 ns, 5 mJ) of DCA (ca. 10^{-5} M) in oxygenated CH_3CN with added BP (0.2M) and azo 1 (0.015 M) resulted in the rapid decay (< 20 ns) of the $BP^{+\cdot}$ absorbance, λ_{obs} = 680 nm. Unfortunately, under our experimental conditions, no concomitant absorption increase was observed for the presumably formed $1^{+\cdot}$. However, under conditions in which $BP^{+\cdot}$ is completely quenched by 1, the addition of trianisylamine (TAA, 3×10^{-4} - 3×10^{-3} M) resulted in the growth of the $TAA^{+\cdot}$ absorption, λ_{max}= 670 nm. The plot of the rate of growth of the $TAA^{+\cdot}$ absorption versus [TAA] is linear with slope of 4×10^9 $M^{-1}s^{-1}$, and an intercept of 4.1×10^6 s^{-1}. This intercept, $k_{frag}(1^{+\cdot})$, corresponds to the sum of all the decay processes of the species which oxidizes TAA. Under similar experimental conditions described above, k_{frag} $(2^{+\cdot})$ = 7.7×10^6 s^{-1} in $10\%CH_3OH/90\%CH_3CN$.

Excitation of DCA (λ_{exc}=430 nm) in degassed CH_3CN with added BP (0.2M) and 1(0.01M) results in two heat depositions, as measured by PAC. We attribute the first, rapid (<10 ns) heat deposition to the formation DCA^- and $1^{+\cdot}$, and the second, slower heat deposition to the decay of $1^{+\cdot}$. The rate constant for the decay of 1^+, $k_{frag}(1^{+\cdot})$ = 2.5×10^6 s^{-1}, is independent of [CH_3OH] and is within experimental error of the value obtained from NAS. Azo cation radical $1^{+\cdot}$ was also generated in several non-nucleophilic solvents using N-methyacridinium as the electron acceptor.[7] The k_{frag} $(1^{+\cdot})$ in these solvents is rather insensitive to solvent polarity and is independent of [CH_3CN] and [CH_3OH].[8] Under similar experimental conditions, k_{frag} $(2^{+\cdot})$ = 5.7×10^6 s^{-1} in $5\%CH_3OH/95\%CH_3CN$.

We attribute the observed fast, first-order decays of both $1^{+\cdot}$ and $2^{+\cdot}$ to initial unimolecular C-N bond dissociation.[9] If correct, then clearly one-electron oxidation *greatly* accelerates the rate of C-N bond fragmentation. The calculated rate constants for the decomposition of 1 and 2 at 298 °C are 3×10^{-15} s^{-1} and 6×10^{-12} s^{-1}, respectively.[10] The decay rates of $1^{+\cdot}$ and $2^{+\cdot}$ are $\geq 10^{18}$ times faster than 1 and 2 at 298 °C. A similar rate acceleration has been previously observed for 1,1'-azonorbornane.[2c]

A thermodynamic arguement for this rate acceleration is that the C-N bond dissociation energy in 1 and 2 is dramatically reduced upon oxidation.[1-2,11] The free energies for decomposition of neutral azoalkanes 1 and 2 at 298 °C, presumably via C-N bond dissociation, are 37.2 and 32.8 kcal/mol, respectively,[10] whereas thermodynamic cycle calculations yield values for $1^{+\cdot}$ and $2^{+\cdot}$ of $\leq$12.7 and $\leq$ 7.2 kcal/mol, a decrease of $\geq$ 24 kcal/mol.[12]

Rapid cation radical fragmentation reactions are potentially useful in the design of highly efficient photoinduced electron transfer reactions. The initial ion radical pair formed upon electron transfer can undergo energy wasting return electron transfer which results in inefficient chemistry. Although $1^{+\cdot}$ and $2^{+\cdot}$ were generated by reaction of 1 and 2 with $BP^{+\cdot}$, azoalkane cation radical fragmentation can potentially compete effectively with return electron transfer. Future mechanistic studies will examine additional azoalkane cation radicals. We hope to determine the temperature dependence on their rate of decomposition to help understand what factors are important in achieving faster fragmentation rates. Preliminary studies indicate that their decomposition is entropy controlled, in contrast to that of their neutral precursors which are enthalpy controlled.

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References and Notes

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3. Compounds 3 and 5 were characterized by ^1H and ^{13}C NMR, GC-MS, high resolution MS (M^+), and IR. Minor products in the oxidation of 1 in CH_3CN included t-butylacetamide and the adduct 4. Adduct 3 (14%) is also formed from oxidation of 1 in 20% CH_3OH. ^1H and ^{13}C NMR analysis of 3 shows a mixture of stereoisomers. Compounds 4 and 6 were characterized as their oxidized anthrone products by ^1H and ^{13}C NMR, GC-MS and high resolution MS (M^+). ^1H NMR analysis of the crude reaction mixtures showed 4 and 6 to be cis/trans mixtures.
4. See for related example involving cation radical cleavage and DCA adduct formation, Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Mattes, S. L.; Todd, W. P. *J. Am. Chem. Soc.*, 1989, *111*, 8973.
5. Quantum yield was determined by *trans*-stilbene/9,10-phenanthrenequinone actinometry. See Bohning, J. J.; Weiss, K. *J. Am. Chem. Soc.*, 1966, *88*, 2893.
6. In CH_3CN (0.1 M $Bu_4N^+PF_6^-$), $E_p(1) = 1.15$ V (SCE), $E_p(2) = 1.20$ V (SCE), $E_p(5) = 1.80$ V (SCE).
7. Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.*, 1991, *113*, 3601.
8. For example, $k_{frag}(1^{+\cdot})$ is 3.3×10^6, 3.4×10^6, and $2.9 \times 10^6\ s^{-1}$ in 1,2-dichloroethane, $CHCl_3$, and C_6H_5Cl.
9. The decay of $1^{+\cdot}$ may involve isomerization to *cis*-$1^{+\cdot}$ and then rapid fragmentation. However, given the thermal lability of the precursor to *cis*-$1^{+\cdot}$, *cis*-1, preparing and determining the decay rate of *cis*-$1^{+\cdot}$ may be difficult. However, the decay of $2^{+\cdot}$ is probably not due to isomerization to trans $2^{+\cdot}$, given the anticipated endothermicity of this reaction.
10. Engel, P. S. *Chem. Rev.*, 1980, *80*, 99. and references therein.
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12. These values are estimated from thermodynamic cycle calculations using the equation $\Delta G^o_{BDE}(CR) = \Delta G^o_{BDE}(N) - E^o_{ox}(N) + E^o_{ox}(tbutyl\cdot)$, where $\Delta G^o_{BDE}(CR)$ and $\Delta G^o_{BDE}(N)^{10}$ are the free energies for bond dissociation for cation radical and neutral precursor, and $E^o_{ox}(N)$ and $E^o_{ox}(tbutyl\cdot)$ are the oxidation potentials of the neutral and the t-butyl radical. This calculation uses $E_p(N)^6$ and $E_{1/2}(tbutyl\cdot) = 0.09$ V vs. SCE (Wayner, D.D.M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* 1988, *110*, 132), and assumes that C-N bond dissociation of $1^{+\cdot}$ and $2^{+\cdot}$ yield the butyl cation/diazeneyl radical intermediate(s) rather than the diazonium cation/butyl radical intermediate(s). In the latter case, $E_{ox}(diazenyl\cdot)$ would be lower that $(tbutyl\cdot)$, which would lower $\Delta G^o_{BDE}(CR)$. Unfortunately, neither $E_{ox}(diazenyl\cdot)$ nor E_{red}(diazonium cation) are known.

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