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Phenyl Substitution Effects on Rate Acceleration of Cation Radical Deazetation of 2,3-Diazabicyclo[2.2.2]oct-2-enes

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Abstract: Under the 9,10-dicyanoanthracene (DCA)-photosensitized electron-transfer conditions 1-phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (1b) and 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (1c) were deazetized with rate constants, k_{-N2} , of ca. 8.4 × 10⁷ and 6.6 × 10¹⁰ s⁻¹, respectively, whereas the parent 2,3-diazabicyclo[2.2.2]oct-2-ene (1a) was not reactive, showing remarkable rate acceleration by the σ (C-N)- π (Ph) orbital interaction due to the phenyl substitution. Copyright © 1996 Elsevier Science Ltd

Recently, much attention has been focused on electron-transfer (ET) deazetations of 2,3-diazabicyclo-[2.2.2]oct-2-enes, potential precursors to cyclohexa-1,4-diyl cation radicals (CR) $(2^{\bullet+})$.¹⁻⁶ However, the deazetations were reported to depend strongly upon the ET conditions employed. Deazetation of the diphenyl derivative (1c) occurred facilely under both the DCA-sensitized and Ce(NH4)₂(NO3)₆ (CAN)-catalyzed ET conditions, ^{1,2} while the parent 1a was deazetized neither by γ -ray irradiation in a Freon matrix, ^{3,4} tris(4-bromophenyl)aminium hexachloroantimonate-catalyzed reaction⁵ nor by photoexcitation of the electron donor-acceptor (EDA) complex with tetracyanoethylene.⁴ In addition, the deazetation product varied with change in the ET deazetation conditions, ¹ while the CAN-catalyzed reaction of 1c gave 1,4-diphenyl-1,3-cyclohexadiene.² In order to gain mechanistic insight into deazetations of 2,3-diazabicyclo[2.2.2]oct-2-enes under ET conditions, we investigated phenyl substitution effects on rate acceleration of the DCA-sensitized CR deazetations of 1a-c and found that the σ (C-N)- π (Ph) orbital interaction has significant impact on the deazetation efficiency.



In Table 1 are shown the Stern-Volmer $(k_q \tau)$ and rate constants (k_q) for the DCA-fluorescence quenching by **1a-c** together with the halfwave oxidation potentials $(E^{\text{ox}}_{1/2})^7$ of **1a-c** in CH₂Cl₂. In spite of large k_q close to the diffusion control rate, the DCA-sensitized photoreaction $(\lambda > 410 \text{ nm})$ of **1a** in CD₃CN, CD₂Cl₂ or C₆D₆ resulted in a quantitative recovery either in the absence or presence of the cosensitizer biphenyl as well as the 2,4,6-triphenylpyrylium tetrafluoroborate-sensitized photoreaction of **1a**.⁸

	$\frac{E_{1/2}^{\text{ox}a}}{\text{V}}$	<u></u> κ _q τ Μ ⁻¹	$\frac{k_{\rm q}}{10^{10}{\rm M}^{-1}{\rm s}^{-1}}$	Ø ^{b)}	$\boldsymbol{\Phi}_{\mathrm{cor}}$	$\frac{k_{\text{bet}}}{10^9 \text{ s}^{-1}}$	$\frac{k_{-N^2}}{10^9 \text{ s}^{-1}}$	
1 a	+1.66	127	1.09	0	0	0.94	~0	
1b	+1.50	134	1.15	0.018	0.031	2.6	0.084	
1c	+1.39	143	1.22	0.55	0.93	5.0	66	

Table 1. Oxidation Potentials ($E^{\text{ox}}_{1/2}$) of **1a-c**, the Stern-Volmer ($k_q \tau$) and Rate Constants (k_q) for the DCA-Fluorescence Quenching, Observed Quantum Efficiencies ($\boldsymbol{\Phi}$) and Corrected Quantum Efficiencies ($\boldsymbol{\Phi}_{\text{oor}}$) for Deazetation and Calculated Rate Constants for BET (k_{bet}) and CR Deazetation (k_{Na}) in CH₂Cl₂

a) vs. SCE, scan rate 100 mV/s. b) [1] =0.01 M.

In contrast, the DCA-sensitized photoreactions of 1b and 1c in CH₂Cl₂ afforded 2-phenyl-1,5-hexadiene (3b) and 3c, respectively, in quantitative yields.⁸ Interestingly, the DCA-sensitized photoreaction of 1b in benzene gave not only 3b (67%) but also 1-phenylbicyclo[2.2.0]hexane (4b, 4%).⁹ Similar results were obtained upon photoexcitation ($\lambda > 410$ nm) of the EDA complexes of **1b-c** and 1,2,4,5-tetracyanobenzene. The corrected quantum efficiencies ($\boldsymbol{\Phi}_{cor}$) for the formation of 3 were determined as $\boldsymbol{\Phi}_{cor} = \boldsymbol{\Phi} / Q_e$ by using observed quantum efficiencies (Φ)¹⁰ and quenching efficiencies ($Q_e = k_q \tau [1] / \{1 + k_q \tau [1]\}$) (Table 1) and provided significant phenyl substitution effects on deazetation of 1, showing that 93% of the ion pair [1c⁺⁺/DCA⁺⁻] afforded 3c whereas most of the ion pair [1a⁺⁺/DCA⁺⁻] decayed to 1a and DCA by back-electron transfer (BET).¹¹ In fact, nanosecond time-resolved laser flash photolysis of an aerated CH₂Cl₂ solution of 1b and N-methylquinolinium tetrafluoroborate (NMO⁺BF₄) in the presence of 2 M toluene gave no transient absorption, whereas that of 1c gave a transient absorption due to $2c^{+}$ at $\lambda_{max} = 482$ nm, which was confirmed by comparison with absorption observed by similar laser flash photolysis of 3c (Fig. 1).¹² Note that this λ_{max} is different from those of the free cumyl cation (326 nm, 390 nm)¹³ and cumyl radical (315 nm),¹⁴ suggesting the through-bond interaction between cation and radical counterparts. A plausible mechanism for the PET deazetation of 1 is shown in Scheme 1. Diazenyl and cyclohexa-1,4-diyl CRs (5^{*+} and 2^{*+}) serve as key intermediates in a stepwise deazetation of 1^{++} . If this mechanism is really operative, $\boldsymbol{\Phi}_{cor}$ can be further represented as $\Phi_{cor} = k_{N_2} / (k_{N_2} + k_{bet})$, in which k_{N_2} and k_{bet} are rate constants of deazetation and BET in [1^{•+}/DCA^{•-}]. By using calculated rate constants, ${}^{15}k_{bet} = 2.6 \times 10^9$ and 5.0×10^9 s⁻¹ for 1b and 1c, respectively, k_{-N_2} were estimated to be 8.4 × 10⁷ s⁻¹ for 1b and 6.6 × 10¹⁰ s⁻¹ for 1c as shown in Table 1. Thus, 1c⁺⁺

Scheme 1









Fig. 1. Nanosecond absorption spectra of an aerated CH_2Cl_2 solutions of 1c (1 mM, top) and 3c (1 mM, bottom) under the NMQ⁺BF₄ (1 mM)-toluene (2 M) cosensitized conditions.

Fig. 2. Energy level diagram for occupied molecular orbitals of **1a-c** calculated by PM3.

undergoes deazetation *ca.* 800 times faster than $1b^{++}$. It is of interest to compare k_{-N_2} of 1^{++} with rate constants of deazetation of the neutral counterparts. The calculated rate constants of thermal deazetations of 1a, 1b and 1c were, respectively, 4.2×10^{-19} , 5.1×10^{-13} and $1.4 \times 10^{-10} s^{-1}$ at 20 °C, ¹⁹ indicating that rate acceleration by the phenyl substitution is more significant in the CR state than the neutral state. It is also noteworthy that deazetations of $1b^{++}$ and $1c^{++}$ took place $>10^{20}$ times faster than those of the neutral counterparts.

One possible explanation for the phenyl substitution effects on CR deazetation is thermodynamics of the initial C-N bond cleavage of 1^{*+} to 5^{*+} . The PM3/UHF calculations suggested that cleavage of $1a^{*+}$ to $5a^{*+}$ is 11.6 kcal/mol endothermic whereas that of $1b^{*+}$ occurs with heat evolution of 6.9 kcal/mol.²⁰ Results of the calculation are in accord with conventional explanation in term of the difference in stability among secondary $(5a^{*+})$ and tertiary $(5b^{*+} \text{ and } 5c^{*+})$ CRs. Furthermore, the PM3 calculation revealed that HOMOs of 1b and 1c are comprised of an antibonding combination of HOMOs of 1a and benzene, whereas their bonding combinations form the third HOMO of 1b (HOMO-2 in Fig. 2) and the fifth HOMO of 1c (HOMO-4). The latter combination is due to the σ (C-N)- π (Ph) orbital interaction, which can diminish the C-N bond order just as hyperconjugation does. A similar but more efficient σ (C-N)- π (Ph) orbital interaction is apparently available for $1b^{*+}$ and $1c^{*+}$, because upon loss of an electron from HOMOs, the HOMO-2 of $1b^{*+}$ and HOMO-4 of $1c^{*+}$ increase in contribution to total MOs as compared with neutral 1b and 1c. Therefore, the more effective rate acceleration by the phenyl substitution in the CR state than the neutral state must be attributed to the more efficient σ (C-N)- π (Ph) orbital interaction.

In conclusion, the observed remarkable rate acceleration for CR deazetations of 2,3-diazabicyclo-[2.2.2]oct-2-enes can be accounted for by the σ (C-N)- π (Ph) orbital interaction due to the phenyl substitution which consequently involves exothermic initial C-N bond cleavage.

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- 7. $E^{0x}_{1/2}$ were estimated as E_{pa} (anodic peak potentials) 0.03 V, which were measured by cyclic voltammetry at a platinum electrode in dry CH₂Cl₂ with 0.1 M *n*-Bu₄NBF₄ as a supporting electrolyte.
- 8. A 0.5 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter ($\lambda > 410$ nm) at 20 °C.
- Selected data of 4b.: Colorless oil. Anal; Calcd. for C₁₂H₁₄; C = 91.08%, H = 8.92%. Obsd.; C = 88.16%, H = 8.71%. HRMS (EI, 70 eV); Calcd. for C₁₂H₁₄; 158.1095. Obsd.; 158.1098. MS (70 eV, *m/z*, %); 158 (M⁺, 13), 143 (8), 130 (32), 129 (35), 115 (100), 104 (39), 91 (38), 77 (45). IR (neat, cm⁻¹); 2920, 1600, 1496, 757, 696. ¹H NMR (200 MHz, CDCl₃); δ_{ppm} 1.95 2.14 (m, 2 H), 2.33 2.64 (m, 6 H), 2.93 3.07 (m, 1 H), 7.10 7.39 (m, 5 H). ¹³C NMR (50 MHz, CDCl₃); δ_{ppm} 24.97 (2 C), 34.56 (2 C), 40.30, 49.11, 124.68 (2 C), 125.28, 128.19 (2 C), 148.68.
- 10. A 3 mL CH₂Cl₂ solution was irradiated (λ = 436 ± 12 nm) at 20 °C with a 500 W Hg-Xe lamp through a cutoff filter (λ > 350 nm), an interference filter (λ max = 437 nm), and an aqueous CuSO4 solution filter.
 [1] = 0.01 M, [DCA] = 1.38 × 10⁻³ M. Aberchrome 540 was used as an actinometer.
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- 12. An excimer laser ($\lambda_{ex} = 308 \text{ nm}$) was used for nanosecond absorption spectrometry. A similar deazetation of 1c took place in CH₂Cl₂ under the NMQ⁺BF₄-toluene cosensitized conditions ($\lambda = 305 \pm 5 \text{ nm}$).
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- 15. The calculated rate constants, k_{bet} , were obtained from the following equations $(1, 2)^{16}$ by using reported parameters in CH₂Cl₂.^{17, 18}

$$k_{\text{bet}} = \left(\frac{4\pi^3}{\hbar^2 \lambda_s k_b T}\right)^{1/2} |\mathcal{V}|^2 \sum_{\omega=0}^{\infty} \left(\frac{e^{-s} S^{\omega}}{\omega!}\right) \exp\left\{-\frac{(\lambda_s + \Delta G + \omega h \nu)^2}{4 \lambda_s k_b T}\right\}$$
(1), $S = \lambda_v / h \nu$ (2)

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- 18. The ΔG_{bet} values for BET in [1^{*+}/DCA^{*-}] in CH₂Cl₂ were estimated by the following equations: $\Delta G_{\text{bet}} = -\{E^{\text{ox}}_{1/2}(1) E^{\text{red}}_{1/2}(\text{DCA}) e^{2}/\epsilon r\}$, where $E^{\text{red}}_{1/2}(\text{DCA}) = -0.89$ V and $e^{2}/\epsilon r = 0.23$ eV.
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- 20. PM3 calculations were carried out by using the MOPAC ver. 6 on a Tektronix CAChe WorkSystem.

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