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Transformation of Electronic Structure of Diaryldiazomethane Radical Cations as Studied by Cyclic Voltammetry

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The anodic oxidation of diaryldiazomethanes has been studied by cyclic voltammetry in CH_2Cl_2 at low temperature. It is shown that the initially formed π-radical cations are converted to σ-radical cations, which have a more negative reduction potential. The rate constant for the transformation of π- to σ-radicals could be determined for the typical case of dimesityldiazomethane by means of digital simulation of the cyclic voltammogram.

The structure and reactivity of diazoalkane radical cations have been attracted much attention.[1-4] Previously, we demonstrated a unique feature on the electronic structure of diazoalkane radical cations on the basis of their ESR spectra[3]; most interesting was that one-electron removal from π-HOMO of aryldiazomethanes resulted in the formation of cation radicals with an electronic configuration of σ-radicals. Here, we wish to report on the first observation, by means of cyclic voltammetry, on the transformation of electronic structures from π- to σ-radical cations.

Previous ESR study[3] revealed that the anodic oxidation of diphenyldiazomethane (**1a**) in CH_2Cl_2 containing 0.1 M $n\text{-}Bu_4NBF_4$ at -30 — -90 °C yielded a relatively long-lived radical cation.[5] However, the low-temperature cyclic voltammetry of **1a** in the same solvent system shows two reduction peaks on the reverse sweep (Fig. 1). The first cathodic peak (b) at + 1.0 V vs. Ag/AgCl is due to the reduction of the initially formed radical cation, which is rapidly converted to another intermediate reducible at a more negative electrode potential (peak (c)).

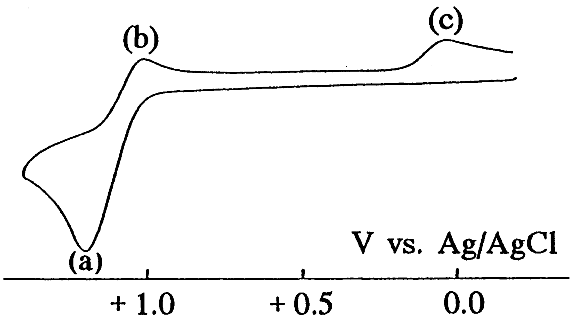


Fig. 1. The cyclic voltammogram of **1a** in CH_2Cl_2 containing 0.1 M $n\text{-}Bu_4NBF_4$ at -78 °C. Sweep rate is 0.1 V/s.

The electronic configurations of diazocompounds and their radical cations are summarized in Scheme 1. Around the oxidation potential (E_1) of diazoalkane (**1**), the removal of one-electron from π-HOMO of **1**[7] affords π-radical cation (**2**), which is reducible to **1** on the reverse sweep (peak (b)). Here, the orbital energy of vacant $\pi_{N\text{-}N}^*$ in **2** is lowered, leading to the internal conversion to more stable σ-radical (**3**).[3] The resulting σ-radical cation (**3**) is no longer reducible at E_1 since the energy of **3** is lower than that of **2**. Thus, the reduction of **3** occurs at a more negative potential (E_2).[8]

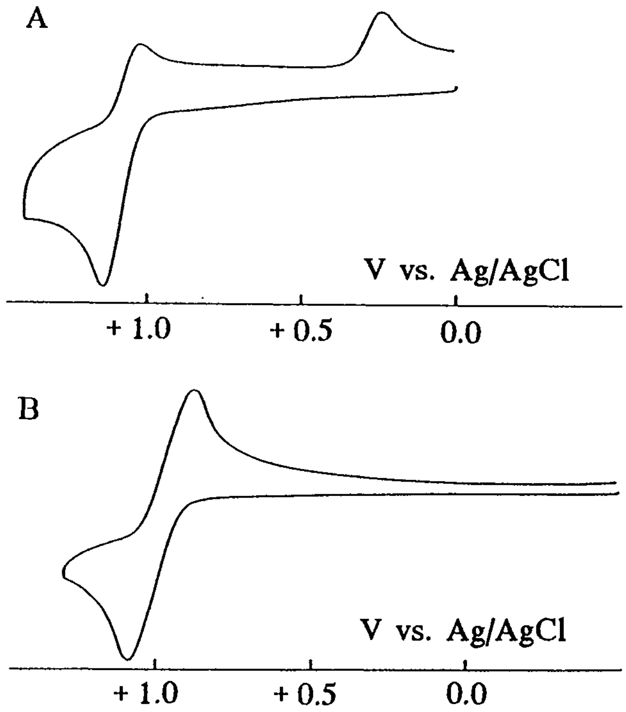
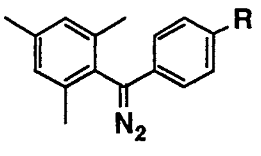


Fig. 2. The cyclic voltammograms of **1d** (A) and **1e** (B) in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 at -78 °C. Sweep rate is 0.1 V/s.

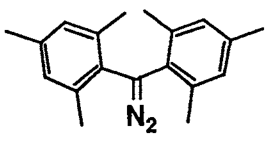
The assignment of peak (c) as the reduction of **3** is also supported by the following results. Similar voltammograms of two reduction peaks were obtained from diazocompounds such as **1b**, **1c**, and **1d** which afforded long-lived σ-radical cations on ESR[9] (Fig. 2A). On the other hand, only one peak of reversible redox couple (Fig. 2B) was observed for the case of **1e** and **1f** which yielded π-radical cations (**2**) solely.[3]

Interestingly, the rate of conversion (**2** → **3**) could be determined by a digital simulation of the voltammograms.[10] According to Scheme 1, the decrease of **2** should be first-order in **2**.The voltammetry of **1a**, however, did not follow a simple first-order kinetics because of inclusion of the dimerization reaction of **2** at low temperature, as noted previously by Parker

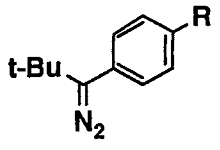


1b : R = H

1c : R = Me

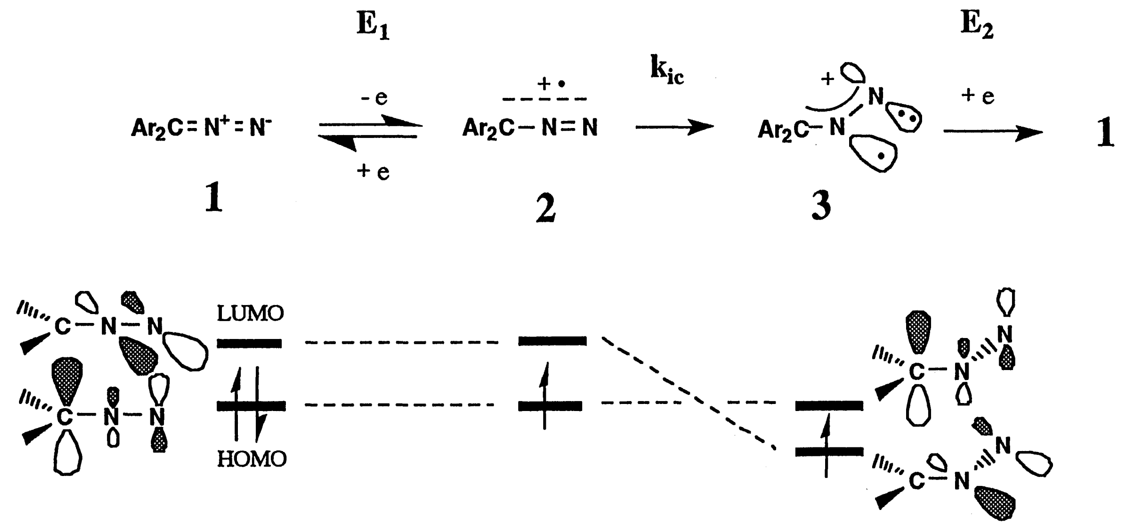


1d



1e : R = Me

1f : R = MeO



Scheme 1 .

and Bethell.[11] This complication could be eliminated by introducing 2,6-substituents in **1** to reduce the second-order reaction of **2**. Thus, the voltammograms of dimesityldiazomethane (**1d**) were nicely simulated with the simple first-order kinetics in **2**. The resulting internal conversion rate constants (k_{ic}) are summarized in Table 1. At each temperature, the rate constants are practically independent of sweep rates or substrate concentrations, suggesting the validity of the assumed mechanism.

Table 1. Cyclic voltammetric data on the conversion of dimesityldiazomethane radical cation (**2d**) a)

Sweep rate	k_{ic} / s^{-1}		
V·s^{-1}	-60 °C	-65 °C	-70 °C
0.1			0.81
0.2		1.7 (2.4) b)	0.90 (0.90) b)
0.5	3.6	2.0 (2.0) b)	0.92 (0.95) b)
1.0	4.1		
av.	3.9 ± 0.3	2.0 ± 0.3	0.90 ± 0.05

a) The CV data of dimesityldiazomethane **1d** in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 under Ar; [**1d**] = 1.0 mM. b) The value in parenthesis are those with [**1d**] = 0.1 mM.

From the temperature effect in Table 1, the activation energy for the internal conversion from **2d** to **3d** is calculated to be ≈54 kJ/mol or ≈13 kcal/mol. The evaluation of this value is not straightforward because such a value has not been observed. But, it is interesting to note here that the relatively high activation energy seems to be reasonable since the conversion is accompanied with a large geometric change in radical cations between **2** and **3**.

Further studies on the relation between the substrate structure and the conversion rate are in progress.

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3) K. Ishiguro, Y. Sawaki, A. Izuoka, T. Sugawara, and H. Iwamura, *J. Am. Chem. Soc.*, **109**, 2530 (1987).

4) V. D. Parker and D. Bethell, *J. Am. Chem. Soc.*, **109**, 5066 (1987).

5) The half-lives of the radical cation were ≈10 s and ≈90 s at -33 and -83 °C, respectively.[3)]

6) Cyclic voltammetric experiments were performed with a Nikko-Keisoku DPGS-1 potentiostat equipped with a NFG-6 function generator. A planar glassy carbon electrode, a Pt plate, and Ag/AgCl were used as working, counter, and reference electrodes, respectively.

7) J. B. Moffat, *J. Phys. Chem.*, **82**, 1083 (1978) and references cited therein.

8) The addition of an electron to the vacant π-orbital (HOMO of **1**) is to produce the diazoalkane in excited state, which should be rapidly deactivated to the ground state **1** or decomposed.

9) The ESR spectra of σ-radical cations of **1b-d** were found to be practically identical with that of diphenyldiazomethane radical cation (**3a**).[3)] The preparative electrolyses of **1b-d** afforded complex mixures including benzophenones and azines as in the case of **1a**.[4)]

10) The voltammograms were acquired with a Gould 4072 digital storage oscilloscope, and transferred to a NEC PC-9801 computer. Background current acquired with a blank solution was subtracted from the rare data. The digital simulation of the voltammograms was carried out with the 2nd-order Runge-Kutta integration and 5-spot approximation for the boundary value expressions; D. Britz, "Digital Simulation in Electrochemistry", Springer Verlag (1988), pp. 63, 74.

11) Parker and Bethell have reported a study on the diaryldiazomethane radical cations in CH_3CN or CH_3OH at room temperature by means of derivative cyclic voltammetry and double potential step chronoamperometry.[4)] But they gave attention only to the first intermediate (**2**) and were unsuccessful to detect the second reduction peak (c) due to **3**.

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