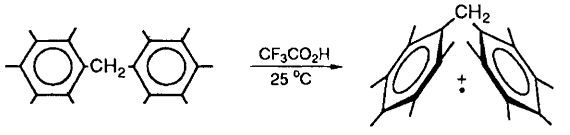
Novel π-Stabilization of Arene Cation Radicals in the Anchimeric Assistance of Electron Transfer

S. Sankararaman, W. Lau and J. K. Kochi*

Department of Chemistry, University of Houston, Houston, TX 77204–5641, USA

Bis(pentamethylphenyl)methane shows exceptional reactivity in electron transfer owing to the formation of a novel π-stabilized cation radical, which is mechanistically delineated by time-resolved spectroscopy.

We report the unusual properties of bis(pentamethylphenyl)methane (decamethyldiphenylmethane; DDM) as an highly active electron donor which is readily converted to the π-stabilized cation radical (DDM$^{\cdot+}$) merely upon dissolution in trifluoroacetic acid [eqn. (1)].† The novel structure of DDM$^{\cdot+}$ is readily deduced from the intense ESR spectrum observed at $<g> = 2.0023$. Thus, Fig. 1(*A*) shows the well resolved hyperfine splittings in DDM$^{\cdot+}$ to consist of triplets ($a_{H} = 5.45$ G) of tridecets ($a_{12H} = 3.34$ G) of tridecets ($a_{12H} = 1.67$ G) (1 G = 10^{-4} T) from the single methylene, four *ortho* and four *meta* groups,‡ respectively, as confirmed in the computer simulated spectrum [Fig. 1(*B*)]. The extensively delocalized structure of DDM$^{\cdot+}$ is reminiscent of the intermolecular analogue,[3] in which hexamethylbenzene cation radical (HMB$^{\cdot+}$) with $a_{18H} = 6.5$ G associates with hexamethylbenzene to form the dimeric (HMB)$_2^{\cdot+}$ with 36 equivalent protons and $a_{36H} \approx 1/2a_{18H}$, as expected for the completely delocalized π-complex, *i.e.* eqn. (2).[4] As such, the average HFS for DDM$^{\cdot+}$ of $\Sigma a/26 = 2.7$ G, which is comparable to $a_{36H} = 3.1$ G for (HMB)$_2^{\cdot+}$, accords with the structure of the delocalized cation radical approximating the cofacial arrangement depicted in eqn. (1).



(1)

The formation of DDM$^{\cdot+}$ in trifluoroacetic acid (eqn. 1) is coincident with the development of strong purple colouration over the course of *ca.* 1 h. The same species is formed in dichloromethane by the ready oxidation of DDM by nitrosonium salts, as shown by the rapid appearance of the diagnostic absorption band at λ_{max} 550 nm ($\varepsilon \approx 2000$ dm^3 mol^{-1} cm^{-1}) and the production of nitric oxide. Reduction of DDM$^{\cdot+}$ can be readily effected by either ferrocene ($E^\circ = 0.40$ V) or *N*-methylphenothiazine (PT, $E^\circ = 0.82$ V);[5] in the latter case, the distinctive absorption bands of the phenothia-

(2)

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† The production of cation radicals by the oxidation of neutral donors in acidic media is a well accepted spectral method.[1]

‡ The small hyperfine splitting (HFS) from the *para* methyl groups of less than the spectral resolution (<0.03 G) has precedent in ref. 2.

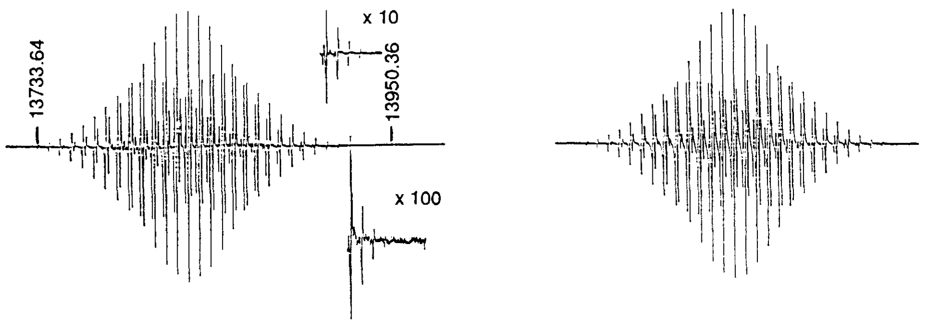


Fig. 1 (*A*) Experimental X-band ESR spectrum of DDM$^{\cdot+}$ obtained from the dissolution of bis(pentamethylphenyl)methane in trifluoroacetic acid. ^{1}H NMR field markers in kHz. (*B*) Computer simulated spectrum of DDM$^{\cdot+}$ based on the HFS listed in the text.

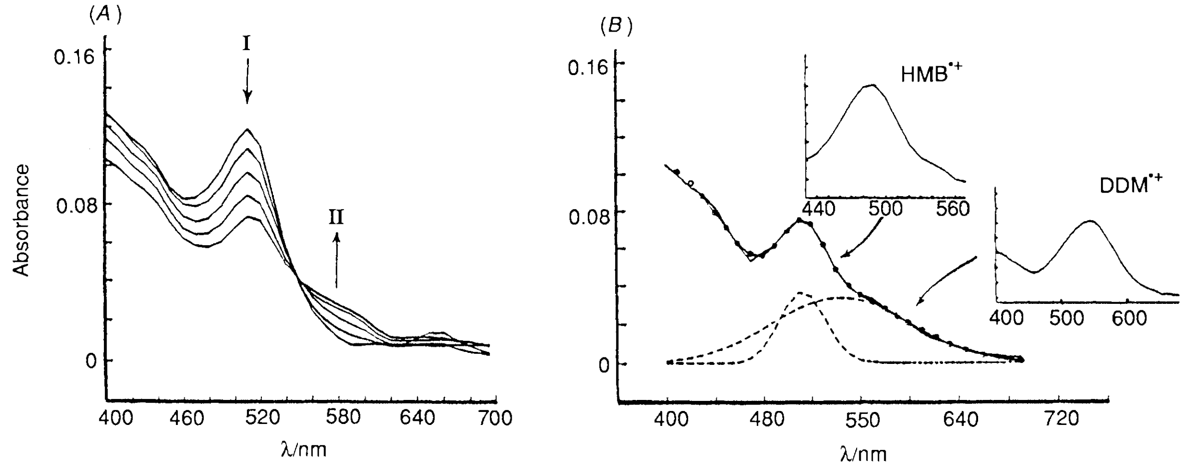
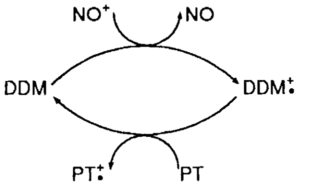


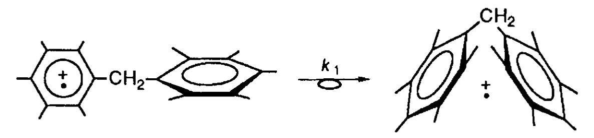
Fig. 2 (*A*) Typical time-resolved difference spectra obtained at t = 0.7, 1.6, 2.4, 3.5 and 4.6 µs following the application of a 10 ns laser pulse at 532 nm to a solution of 5 mmol dm^{-3} DDM and 400 mmol dm^{-3} $C(NO_2)_4$ in dichloromethane. (*B*) Gaussian deconvolution of the 4.6 µs spectrum with the absorption spectrum of HMB$^{\cdot+}$ (inset), DDM$^{\cdot+}$ (inset), and $C(NO_2)_3^-$ (with λ_{max} at 350 nm[7] not shown). The fit of the calculated (-O-O-O-) to the experimental spectrum (———) is included in the envelope.



(3)

zinium ion at λ_{max}/nm 441 (3630), 512 (9120) and 760 (1202)[6] together with the quantitative recovery of DDM allowed the redox stoichiometry to be established as that in eqn. (3).

The dynamics of the π-stabilization of DDM$^{\cdot+}$ were clearly elucidated by direct, time-resolved spectroscopic methods based on previous studies of the photoexcitation of the charge-transfer (CT) complexes of various arene donors with tetranitromethane.[7] Pertinent to this study, such a photoinduced electron transfer leads directly to the unrelaxed cation-radical of the DDM donor by a vertical (Franck–Condon) transition.[8] Thus, Fig. 2(*A*) shows the series of transient spectra obtained subsequent to the 532 nm excitation of the CT complex [DDM, $C(NO_2)_4$] in dichloromethane with the 10 ns (full width at half maximum, second harmonic) pulse from an Nd^{3+} YAG laser. The initial time-resolved spectrum (in the spectral region between 400 and 700 nm) consisted of a prominent absorption band **I** with λ_{max} = 510 nm which disappeared with a first-order rate constant $k_1 = 2.2 \times 10^5\,s^{-1}$. The decay of **I** was accompanied by the simultaneous



(4)

appearance of a new spectral band **II** with a well defined isosbestic point at 548 nm to afford the final transient spectrum with λ_{max} = 550 nm that is clearly associated with DDM$^{\cdot+}$. The gaussian deconvolution of the transient spectrum at an intermediate point in the decay consisted of the simple superposition of the spectral bands **I** and **II**, as shown in Fig. 2(*B*). This, coupled with the identical first-order rate constant for the growth of **II**, indicated the direct conversion (to a single species) of the first-formed (unrelaxed) intermediate, which we assign to the cation radical of DDM localized on a single aromatic ring since it bears a direct spectral resemblance to HMB$^{\cdot+}$ with λ_{max} = 500 nm (ε 2000 dm^3 mol^{-1}).[7] Accordingly, the spectral evolution described in Fig. 2(*A*) represents the formation of the π-delocalized DDM$^{\cdot+}$ *via* the anchimeric relaxation of the transient arene cation radical by an attached, pendant arene. The rather slow first-order rate constant of $k_1 \approx 10^5\,s^{-1}$ for this transformation can be largely ascribed to the steric hindrance§ encountered

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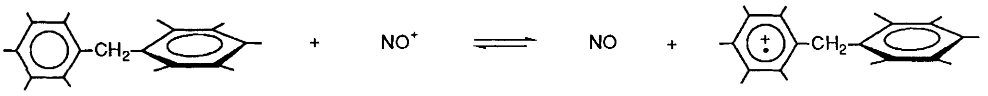
§ The first-order rate constant for k_1 corresponds to an activation energy of ≈ 8 kcal mol^{-1} (by taking the preexponential to be ≈ 10^{11}).



(5)

by two pairs of *ortho*-methyl substituents which must pass each other as the bisected form (pertinent to ground state of DDM[9]) is transformed to the stable cofacial arrangement of the benzenoid rings in DDM^+, *i.e.* eqn. (4).

The driving force of $-\Delta G \approx 10$ kcal mol^{-1} (1 cal = 4.184 J) for the structural transformation of the cation radical in eqn. (4) is indicated by transient electrochemical measurements for the one-electron oxidation of DDM, which occurs in dichloromethane at $E = 1.55$ V, and the reverse reduction of $DDM^{\cdot+}$ at a substantially shifted potential of $E = 0.95$ V.[10] Such a magnitude of $-\Delta G$ accounts for the ready oxidation of DDM by NO^+ in eqn. (3) under conditions in which HMB is unreactive. Since both of these donors have comparable values of the vertical ionization potential (HMB, 7.89 eV and DDM, 7.80 eV),[11] the thermal (adiabatic) electron transfer process is best formulated as a reversible electron transfer from one ring of DDM, *i.e.* eqn. (5), that is actually driven to completion by the π-stabilization depicted in eqn. 4.[12] This EC formulation is supported by the observed rate constant $k_2 \approx 3$ dm^3 mol^{-1} s^{-1} which is diminished by a factor of ten in the presence of added ≈ 0.05 dm^{-3} mol^{-1} nitric oxide.

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