Supporting Information

for

Angew. Chem. Int. Ed. Z52990

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5-Dehydro-1,3-quinodimethane: A Hydrocarbon with an Open-Shell Doublet Ground State

by

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Experimental procedures and results for the kinetic method determination of the electron affinity of DMX
All experiments were carried out using a flowing afterglow – triple quadrupole instrument that has been described in detail previously \[1\]. The EA of DMX was determined by using the kinetic method developed by Cooks and co-workers \[2\], with full entropy analysis \[3\]. The experiment involves the measurement of the branching ratio for collision-induced dissociation (CID) of the SO$_2$ adducts of DMX$^-$, prepared by direct addition of DMX$^-$ with SO$_2$ (Eq. S1).

$$\text{DMXSO}_2^- \rightleftharpoons \text{DMX}^- + \text{SO}_2^- \quad \text{(Eq. S1)}$$

In the full analysis, the EA of DMX is related to the branching ratio for CID of DMXSO$_2^-$, $R_{\text{DMX},E}$, at the selected collision energy, $E$, the branching ratios for CID of reference ions, $R_{B_i,E}$ and the electron affinities of the references, $EA(B_i)$ according to Eq. S2, where $T_{\text{eff},E}$ is the “effective temperature” \[4\] of the dissociation at collision energy, and $\Delta S$ reflects the difference in the activation entropies in the dissociation reactions of SO$_2$ adduct ions \[5\]. The quantitative relationship between the branching ratio, $R$, and the electron affinity is established by calibration by using phenyl (EA = 25.3 ± 0.1 kcal mol$^{-1}$) \[6\], 4-chlorophenyl (EA = 32.8 ± 3.2 kcal mol$^{-1}$) \[7\], and $\alpha$-naphthyl (EA = 32.4 ± 0.3 kcal mol$^{-1}$) \[8\] radicals as references.

$$\ln \left( \frac{R_{\text{DMX}}}{R_{B_i}} \right)_E = \frac{EA(\text{DMX}) - EA_{\text{ave}} + T_{\text{eff},E} \Delta S}{RT_{\text{eff},E}} - \frac{EA(B_i) - EA_{\text{ave}}}{RT_{\text{eff},E}} \quad \text{(Eq. S2)}$$

According to Eq. 8, a plot of $\ln \left( \frac{R_{\text{DMX}}}{R_{B_i}} \right)_E$ versus $EA(B_i) - EA_{\text{ave}}$ at a given energy has a slope $m_E = -1/RT_{\text{eff}}$ and an intercept $y_E = \left[ EA(\text{DMX}) - EA_{\text{ave}} + T_{\text{eff}} \Delta S \right] / RT_{\text{eff}}$, where $R$ is the gas
constant. The term $EA_{ave}$ is the average electron affinity of the references, and is included to remove an artificial correlation between the slope and intercept in this analysis [9]. A second plot of $y_E$ versus $-m_E$ has a slope $EA(DMX) - EA_{ave}$ and an intercept of $\Delta S/R$.

Measured branching ratios and representative plots of $\ln\left(\frac{R_{DMX}}{R_{Bi}}\right)$ versus $EA(B_i) - EA_{ave}$ are shown in Figs. S1 and S2. The second regression plot, used to determine the electron affinity, is shown in Fig. S3. The slope of the plot, $-5.3 \pm 0.4$ kcal mol$^{-1}$, when added to $EA_{ave}$, $30.2 \pm 1.2$ kcal mol$^{-1}$, yields $EA(DMX) = 24.9 \pm 2.0$ kcal mol$^{-1}$, where the uncertainty includes the average error of the references, the error in the slope of the second regression plot (the 90% confidence limit [9]), and a 40% error in the effective temperature [3, 4]. The intercept of the second regression is $0.68 \pm 0.25$, yielding $\Delta S = 1.4 \pm 0.5$ cal mol$^{-1}$ K$^{-1}$, indicating only small differences in the activation entropies among the dissociation reactions.

References for Supporting Material

**Fig. S1.** Plot of $\ln R$ versus center-of-mass frame-of-reference collision energy for Collision Induced Dissociation of SO$_2$ adducts of DMX$^-$ and reference ions.
Fig. S2. Kinetic method plots of $\ln\left(\frac{R_{DMX}}{R_{B_i}}\right)$ versus EA - EA_{avg} at collision energies 5.0, 6.5, and 8.0 eV.
Fig. S3. Second regression plot of \([\text{EA(DMX)} - \text{EA}_{\text{ave}} + T_{\text{eff}}\Delta S]/R_{\text{eff}}\) vs \(-1/RT_{\text{eff}}\) for the electron affinity measurement of DMX. The slope of the plot corresponds to \(\text{EA(DMX)} - \text{EA}_{\text{ave}}\), where \(\text{EA}_{\text{ave}}\) is the average electron affinity of the reference radicals (30.2 ± 1.2 kcal mol\(^{-1}\)).

\[
\gamma_E = \frac{[\text{EA(DMX)} - \text{EA}_{\text{ave}} + T_{\text{eff}}\Delta S]}{R_{\text{eff}}},
\]

Slope: \(-5.3 \pm 0.4\) kcal mol\(^{-1}\)
Intercept: \(+0.68 \pm 0.25\)
\(r^2 = 0.85\)