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Homolytic vs Heterolytic C−H Bond Cleavage in Alkylaromatic Radical Cations. Formation of Diarylmethyl Cation in the Photoinduced Electron Transfer Reaction of Bis(4-methoxyphenyl)methane Sensitized by Chloranil

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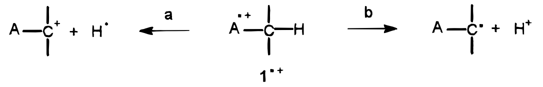
In the generic radical cation $\mathbf{1}^{\bullet+}$, the cleavage of the C−H bond is much easier than in the neutral parent compound. The cleavage of this bond can occur homolytically or in a heterolytic fashion, as shown in Scheme 1.[2]

Scheme 1



Path (b) is the one generally observed in solution,[3] and accordingly, radical cations $\mathbf{1}^{\bullet+}$ represent a very interesting class of strong carbon acids, whose kinetic and thermodynamic acidity is the object of continuous investigation.[4,5] The preference for the heterolytic pathway is so strong that it is also observed when the radical cation reacts with a radical anion, a typical situation in photoinduced electron transfer reactions.[6] The possibility of the alternative path (a) involving a hydrogen atom transfer reaction was rarely considered and, as far as we know, never demonstrated.[7,8]

In this context, the results presented here of a study of the photoinduced electron transfer reactions of bis(4-methoxyphenyl)methane, $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$, sensitized by chloranil (CA) in MeCN, clearly indicating the occurrence of a hydrogen atom transfer from the radical cation to the chloranil radical anion ($\text{CA}^{\bullet-}$), appear certainly of interest. These results are presented here.

Photolysis by laser excitation ($\lambda_{\text{exc}} = 355$ nm)[10] of an Ar-saturated MeCN solution of CA (3.6×10^{-3} M) and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ (1.0×10^{-2} M) produced the time-resolved spectra shown in Figure 1. The spectrum recorded 0.4 μs after the laser pulse shows clear absorptions at 320 and 450 nm, attributed to $\text{CA}^{\bullet-}$ ($\lambda_{\max} = 320$, 425, and 450 nm)[12] and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ ($\lambda_{\max} = 450$ nm),[5] formed by reaction of the excited triplet chloranil (too short-lived to be detected under these experimental conditions) with $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$. Very surprisingly, however, the decay of $\text{CA}^{\bullet-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ did not lead to the formation of $\text{CAH}^{\bullet}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet}$, the products of the expected proton transfer reaction (eq 1). Accordingly, no rise in absorption was observed at 350−360 nm, the wavelength region where both $\text{CAH}^{\bullet}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet}$ are reported to absorb.[11a,13,14]

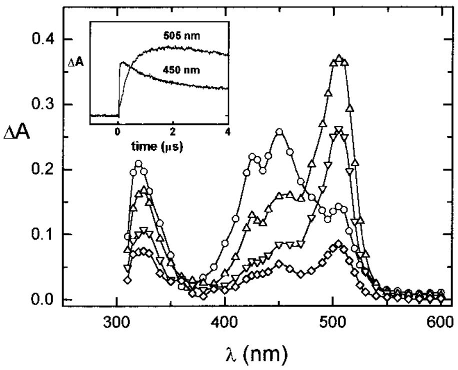


Figure 1. Time-resolved absorption spectra of CA (3.6×10^{-3} M) and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ (1.0×10^{-2} M) in Ar-saturated MeCN recorded 0.4 (○), 3.4 (Δ), 12 (∇), and 30 (◇) μs after the laser pulse ($\lambda_{\text{exc}} = 355$ nm, pulse width of 7 ns and laser energy of ca. 3 mJ pulse^{-1}). Inset: kinetics recorded at 450 and 505 nm.

$$\text{CA}^{\bullet-} + (4\text{-MeOPh})_2\text{CH}_2^{\bullet+} \rightarrow \text{CAH}^{\bullet} + (4\text{-MeOPh})_2\text{CH}^{\bullet} \quad (1)$$

$$\text{CA}^{\bullet-} + (4\text{-MeOPh})_2\text{CH}_2^{\bullet+} \rightarrow \text{CAH}^{-} + (4\text{-MeOPh})_2\text{CH}^{+} \quad (2)$$

Instead, $\text{CA}^{\bullet-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ decayed, by second-order kinetics ($t_{1/2} = 7.7$ μs), leading to the buildup of a very intense signal at 505 nm (see inset of Figure 1), attributed to $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{+}$ on the basis of literature data.[14] In line with this attribution, the decay rate of the 505 nm transient (a first-order process with $k = 4.5 \times 10^4$ s^{-1}) is unaffected by oxygen, but strongly increased by addition of water.[14,15] It seems therefore reasonable to suggest that the reaction between $\text{CA}^{\bullet-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ involves a hydrogen atom transfer process from the radical cation to $\text{CA}^{\bullet-}$ to produce a carbocation, as described in eq 2. In line with this hypothesis, the spectrum recorded at 30 μs also clearly shows the presence of CAH^{-} which absorbs at 320 and 450 nm.

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[2] Baciocchi, E. *Acta Chem. Scand.* **1990**, *44*, 645 and references therein.

[3] See for example: Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 904−908 and references therein.

[4] Anne, A.; Hapiot, P.; Moiroux, J.; Neta, P.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 4694−4701 and references therein.

[5] Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290.

[6] Albini, A. Advances in Electron Transfer Reactions. *Top. Curr. Chem.* **1993**, *168,* 1−46. Albini, A. In *Photoinduced Electron Transfer;* Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, Chapter 4.3. Hoshino, M.; Shizuka, H. In *Photoinduced Electron Transfer;* Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, Chapter 4.5. Lewis, F. D. *Acc. Chem. Res.* **1986**, *19,* 401−405.

[7] Anne, A.; Moiroux, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1993**, *115,* 10224−10230. Ci, X.; Silveirada Silva, R.; Nicodem, D.; Whitten, D. G. *J. Am. Chem. Soc.* **1988**, *111,* 1337−1343. Ci, X.; Whitten, D. G. In *Photoinduced Electron Transfer;* Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, Chapter 4.9. Kuder, J. E.; Limburg, W. W.; Stolka, M.; Turner, S. R. *J. Org. Chem.* **1979**, *44,* 761−766.

[8] The possibility of a hydrogen atom transfer was mainly suggested for amine radical cations which are relatively weak carbon acids, whereas the homolytic bond dissociation energy of the C−H bond is very low.[9]

[9] Nillsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986**, *108,* 4879−4881.

[10] At this wavelength and at the concentrations used in our experimental conditions, excitation concerns only uncomplexed chloranil and not the EDA complex formed by CA and the substrate.[11]

[11] (a) Kobashi, H.; Funabashi, M.; Kondo, T.; Morita, T.; Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1984**, *57,* 3557. (b) Perrier, S.; Sankaraman, S.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 825.

[12] Andree, J. J.; Weill, G. *Mol. Phys.* **1968**, *15*, 97.

[13] Kobashi, H.; Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1986**, *59,* 1975.

[14] Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918.

[15] In extremely anhydrous MeCN, the carbocation follows a second-order decay.[14] Since $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOH}$ was the only product observed by us in steady-state photolysis, probably the amount of water in our medium (ca. 5×10^{-3} M) is sufficiently high to produce first-order kinetics.

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Even though this result was unexpected, it must be pointed out that it could be predicted, at least on thermodynamic grounds. Accordingly, on the basis of appropriate thermochemical cycles, the $\Delta G°$ value for reaction 2 should be ≤ -29 kcal mol^{-1},[16] i.e., largely more negative than the value ($\Delta G° = -16.8$ kcal mol^{-1}) calculated for the proton transfer reaction (eq 1).[18] Thus, in this system, hydrogen atom transfer is thermodynamically favored over proton transfer.

The possibility that the carbocation is formed by reaction 1, followed by the electron transfer reaction of the carbon radical ($E° < 0.16$ V vs NHE)[16,17b] with ground-state chloranil ($E° = 0.254$ V vs NHE)[19b] is considered unlikely as no change in the formation rate of the carbocation was observed by increasing the CA concentration. Moreover, the diarylmethyl cation is formed with the same efficiency both in the absence and in the presence of oxygen.[20] If the carbocation would be formed from the carbon radical, the efficiency of its formation should be affected by the presence of oxygen, which is expected to trap the carbon radical (vide infra). Finally, CAH$^{\bullet}$ and its decay should be observed in the spectrum, which is not the case.

Very interestingly, a different situation was found when the laser photolysis of $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ was performed in CH_2Cl_2. The time-resolved spectra obtained in this solvent are reported in Figure 2. The formation of $\text{CA}^{\bullet-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$, both absorbing at 450 nm, was again observed. Even though the absorptions of these two species are difficult to distinguish, the first-order decay of the 450 nm absorption ($k \approx 3 \times 10^7$ s^{-1}; see inset of Figure 2) is fully consistent with the radical ions $\text{CA}^{\bullet-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ decaying as a bound pair. The absorption at 450 nm decreases and is replaced (after about 3 μs) by that of CAH$^{\bullet}$ ($\lambda_{\max} = 360$, 420, and 435 nm)[11a,13] and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet}$ ($\lambda_{\max} = 350$ nm).[14] Thus, in CH_2Cl_2, the radical cation undergoes a proton transfer reaction (eq 1), *and not* a hydrogen atom transfer reaction (eq 2), as observed in MeCN. However, the decrease in absorption at 350−360 nm was accompanied by the buildup of an absorption at 515 nm, attributed to the diarylmethyl cation. In line with this attribution, water accelerated the decay rate of the 515 nm absorption. First-order kinetics were observed, and the rate was found to depend on the concentration of CA, which suggests that the carbocation is formed by the reaction between the carbon radical and ground-state CA.[22] In line with this conclusion, the formation of the carbocation at 515 nm was no longer observed in the presence of O_2, which traps the carbon radical (the shape of the absorption band centered at 350 nm also changed). A linear plot between the first-order rate constant for the formation of the carbocation and the CA concentration was obtained, from which a second-order rate constant of 6×10^7 M^{-1} s^{-1} for the reaction between the carbon radical and CA was calculated.

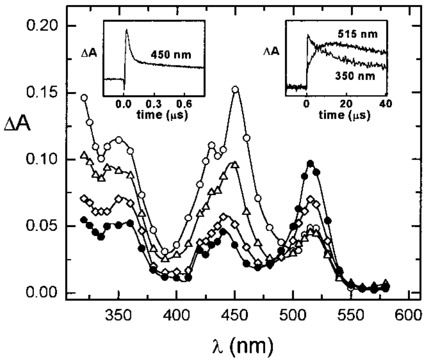

Figure 2. Time-resolved absorption spectra of CA (4.0×10^{-3} M) and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ (1.0×10^{-2} M) in Ar-saturated CH_2Cl_2 recorded 0.1 (○), 0.4 (Δ), 2.6 (◇), and 8 (●) μs after the laser pulse ($\lambda_{\text{exc}} = 355$ nm, pulse width of 7 ns and laser energy of ca. 3 mJ pulse^{-1}). Insets: kinetics recorded at 350, 450, and 515 nm.

Thus, a mechanistic changeover, from homolytic to heterolytic C−H bond cleavage in the radical cation, is observed on going from MeCN to CH_2Cl_2. This is probably due to the much stronger basicity of $\text{CA}^{\bullet-}$ in the latter solvent where, moreover, $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ is deprotonated within a radical−ion pair. In CH_2Cl_2, therefore, reaction 1 may become favored over reaction 2. An increase in the reduction potential of $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$ on going from MeCN to CH_2Cl_2 might also play a role.

In conclusion, it has been clearly shown, for the first time, that an alkylaromatic radical cation can undergo homolytic breaking of the C_α−H bond when it reacts with $\text{CA}^{\bullet-}$ in MeCN. The low basicity of $\text{CA}^{\bullet-}$ in MeCN (pK_a = 6.8)[18] and the substantial spin density on the oxygen atoms probably play a fundamental role in this respect, as well as, of course, the reduction potential of the formed carbocation. Thermochemical calculations indicate that in MeCN the homolytic process remains thermodynamically favored with respect to the heterolytic one as long as the reduction potential of the formed carbocation is <0.7 V vs NHE. Thus, the homolytic process may be much more frequent than it was hitherto thought,[23] and chloranil-sensitized photolyses in MeCN might represent an attractive new method for the production and the study of a significant number of arylmethyl cations. We are presently working to test this possibility.

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[16] Calculated from the equation $\Delta G°(\text{reaction 2}) = \Delta G_{\text{hom}}(\text{Ar}_2\text{CH}{-}\text{H}^{\bullet+}) - \Delta G_{\text{hom}}(\text{CA}{-}\text{H}^-)$ (Ar = 4-MeOC$_6$H$_4$). $\Delta G_{\text{hom}}(\text{Ar}_2\text{CH}{-}\text{H}^{\bullet+})$ is the Gibbs energy for the homolytic cleavage of the C−H methylene bond in the substrate radical cation. Its value was estimated at 25 °C by the equation $\Delta G_{\text{hom}}(\text{Ar}_2\text{CH}{-}\text{H}^{\bullet+}) = 2.3RT\text{p}K_a(\text{Ar}_2\text{CH}_2^{\bullet+}) - 23.06E°(\text{H}^+/\text{H}^{\bullet}) + 23.06E°(\text{Ar}_2\text{CH}^+/\text{Ar}_2\text{CH}^{\bullet})$; the value of p$K_a(\text{Ar}_2\text{CH}_2^{\bullet+})$, −5.5, was calculated as already described[5] but using the most recently reported $E°(\text{H}^+/\text{H}^{\bullet})$ value in MeCN (−1.77 V vs NHE).[17a] Since the oxidation potential for $(4\text{-MeOC}_6\text{H}_4)\text{PhCH}^{\bullet}$ is 0.16 V,[17b] a substantially lower value is expected for the oxidation potential of $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet}$; thus, $\Delta G_{\text{hom}}(\text{Ar}_2\text{CH}{-}\text{H}^{\bullet+})$ should be <37 kcal mol^{-1}. The value of $\Delta G_{\text{hom}}(\text{CA}{-}\text{H}^-)$, the Gibbs energy for the homolytic O−H bond cleavage in CAH$^-$, was taken equal to the value (66.3 kcal mol^{-1}) evaluated in DMSO.[17c]

[17] (a) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287−294. (b) Johnston, L. J.; Kanigan, T. *J. Am. Chem. Soc.* **1990**, *112*, 1271−1273. (c) Cheng, J.-P.; Handoo, K. L.; Xue, J.; Parker, V. D. *J. Org. Chem.* **1993**, *58*, 5050−5054.

[18] Calculated from the equation $\Delta G°(\text{reaction 1}) = 2.3RT[\text{p}K_a(\text{Ar}_2\text{CH}_2^{\bullet+}) - \text{p}K_a(\text{CAH}^{\bullet})]$. p$K_a(\text{Ar}_2\text{CH}_2^{\bullet+})$ is as above, and p$K_a(\text{CAH}^{\bullet})$ in MeCN, 6.8, was calculated at 25 °C by the equation $\text{p}K_a(\text{CAH}^{\bullet}) = (1/2.3RT)[\Delta G°(\text{CA}{-}\text{H}^{\bullet}) + 23.06E°(\text{H}^+/\text{H}^{\bullet}) - 23.06E°(\text{CA}/\text{CA}^{\bullet-})]$. $\Delta G°(\text{CA}{-}\text{H})$ is estimated to be 56 kcal mol^{-1} [the BDE for (CA−H$^{\bullet}$) (64 kcal mol^{-1})[19a] minus the entropy factor (8 kcal mol^{-1})],[5] $E°(\text{H}^+/\text{H}^{\bullet})$ is as above, and $E°(\text{CA}/\text{CA}^{\bullet-})$ is 0.254 V (vs NHE in MeCN).[19b]

[19] (a) Friedrich, L. E. *J. Org. Chem.* **1983**, *48*, 3851. (b) Penn, J. H.; Deng, D.-L. *Tetrahedron* **1992**, *48*, 4823−4830.

[20] By considering that the ϵ values (M^{-1} cm^{-1}) are 10^5 for the carbocation,[14] 10^4 for $\text{CA}^{\bullet-}$,[12] and 10^3 for the radical cation,[21a] respectively, it has been estimated that the yield in carbocation from $\text{CA}^{\bullet-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ is around 13%. Probably, the hydrogen atom transfer reaction competes with diffusive re-encounter of the radical cation with the radical anion whose rate has been estimated to be 2×10^{10} M^{-1} s^{-1},[21b] followed by back electron transfer.

[21] (a) Sehested, K.; Holcman, J.; Hart, J. *J. Am. Chem. Soc.* **1977**, *81*, 1363. (b) Gan, H.; Leinhos, U.; Gould, I. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1985**, *99*, 3566.

[22] (a) At present, the possibility that, at least in part, the carbocation is also formed by reaction of CAH$^{\bullet}$ and the carbon radical cannot be excluded. (b) Even though the yield in carbocation from $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet}$ is difficult to estimate due to the overlap of several absorptions at 350 nm, it is quite low. Therefore, it is possible that the reaction of the radical with CA competes with radical−radical reactions leading to the adduct between MPM and CA, $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOC}_6\text{Cl}_4\text{OH}$, which, accordingly, is the main reaction product in steady-state photolyses in CH_2Cl_2.

[23] The homolytic process may escape detection if a carbocation is formed whose absorption falls outside the investigated region of the spectrum or overlaps with other signals.