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Dynamics of Proton Transfer at Nonactivated Carbons from Laser Flash Electron Photoinjection Experiments

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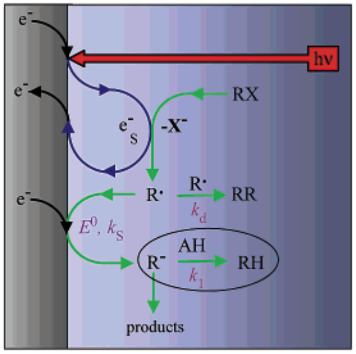
The dynamics of proton exchange at carbon atoms have attracted sustained attention over the years for at least two reasons. One is that, in the examples investigated so far, the protonation/deprotonation reaction is characterized by a substantial intrinsic barrier, much larger than when proton exchange takes place at heteroatoms such as oxygen and nitrogen. The second reason is that, although some progress has been made in the identification of the ingredients of proton exchange intrinsic barriers,[2] an unambiguous and detailed comprehension of the phenomenon is still lacking. Deprotonation of carbon−hydrogen bonds has so far required some form of activation of the carbon atom for the reaction to be amenable to thermodynamic and kinetic characterization. In this connection, there have been two main ways for making carbon-bonded hydrogens more acidic. One consists of decreasing the electron density on the carbon atom by means of an electron-withdrawing group directly borne by the carbon or located in a conjugated position to it on an unsaturated substituent.[2a,3−5] A similar effect is obtained by removing one electron from a nonactivated organic molecule and observing the acidity of the cation radical thus formed.[6]

The lack of a comprehensive model calls for an increased gathering of experimental data in the hope that empirical trends will emerge suggesting new directions to theoretical investigations. In this connection, it would certainly be helpful to complement the existing information by data involving nonactivated carbons. The main difficulty encountered in the investigation of such systems is the poor acidity of the carbon acid form or, equivalently, the extreme instability of the conjugated base. We propose to gather this information by application of laser flash electron photoinjection. The principle of the experiment is summarized in Scheme 1. Electrons are injected in solution by irradiation of the electrode with a laser flash. After a quick thermalization, they react with a rapidly or concertedly cleaving substrate RX, thus producing the radical R•.[7] Thus, shortly after the end of the laser pulse, a thin layer (on the order of 30−100 Å thick) of radicals (surface concentration on the order of 10^{-13} mol/cm^2) has built up at the electrode surface. The variation of the photoinduced charge flowing through the electrode with the electrode dc potential allows the construction of a "polarogram" of the radical that represents its reduction into the corresponding carbanion. These polarograms are S-shaped curves relating the number of electrons per molecule of radical, *n*, to the electrode potential, *E*. Typical examples are given in Figure 1, where the polarograms obtained for the electrochemical reduction of the diphenylmethyl radical produced by the reaction of diphenylmethyl chloride by photoinjected electrons are shown at two different measurement times in the absence and presence of methanol.

Scheme 1. Principle of an Electron Photoinjection Experiment



The half-wave potential, $E_{1/2}$ (potential where *n* is one-half of its limiting value), is a measure of the reducibility of the radical. It is not simply equal to the standard potential, E^0, of the R•/R$^-$ couple. It may indeed also be influenced by the kinetics of electron transfer and of reactions involving the radical (dimerization, in most cases) and the carbanion. The latter species may react spontaneously with the solvent and with impurities present, but also with purposely added acids, thus opening an opportunity to derive the corresponding rate data from the half-wave potential. While the preceding applications of electron photoinjection were aiming at the extraction of the standard potential from the raw data,[7a,b] the method we propose requires the extraction of the protonation rate constant from the $E_{1/2}$ values and their variation with time and acid concentration. Typical variations of the half-wave potential with time and acid concentration are shown in Figure 2a for the reaction of the diphenylmethyl carbanion with methanol. The pertinent thermodynamic and kinetic constants, and particularly the protonation rate

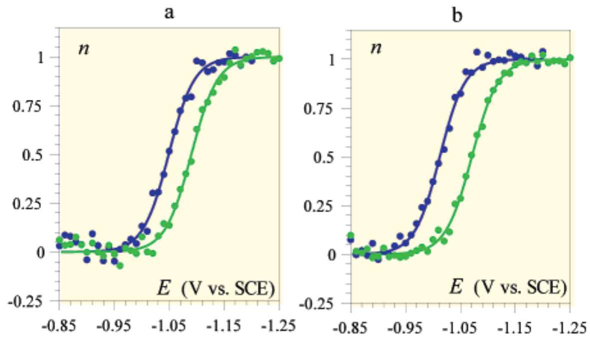


Figure 1. Polarograms obtained for the electrochemical reduction of the diphenylmethyl radical produced by the reaction of diphenylmethyl chloride (30 mM) by photoinjected electrons in dimethylformamide (DMF) + 0.1 M Et_4NClO_4 at 22 °C are shown at two different measurement times (green, 7 ms; blue, 500 ms) in the absence (a) and presence of 81.5 mM methanol (b). *n* is an overall number of electrons featuring the outcome of the chemical fate of the radical.

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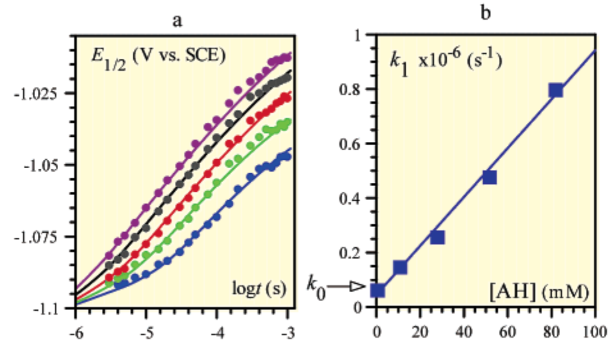

Figure 2. Protonation of the diphenylmethyl carbanion by methanol in DMF + 0.1 M Et_4NClO_4 at 22 °C. (a) Variations of the half-wave potential of the diphenylmethyl radical with time for increasing concentrations of methanol added, from bottom to top: 0, 10.3, 27.4, 51.2, 81.5 mM. (b) Pseudo-first-order rate constant as a function of methanol concentration.

constant, are extracted from the raw data according to the following procedure. In the absence of purposely added acid, the $E_{1/2}$ versus log t curve shows an inflection point in the middle of the time window and a leveling off at long times. At short times, electron transfer controls the overall kinetics, whereas the kinetic control shifts to the follow-up reaction (k_0) at longer times. The leveling off observed at the lower edge of the time window features the interference of the dimerization of the diphenylmethyl radicals (k_d). Because these three segments are distinct, simulating the reaction kinetics[7c] affords the electron-transfer standard rate constant ($k_S D^{-1/2} = 2200\ s^{-1/2}$, where D is the diffusion coefficient of the radical),[8] the rate constant for the decay of the carbanion ($k_0 = 5 \times 10^4\ s^{-1}$), and the dimerization rate constant of the radical ($k_d = 6 \times 10^8\ M^{-1}\ s^{-1}$). The amount of radicals generated by the laser pulse, which is required for the derivation of k_d, was obtained from the measurement of the photoinjected charge and found to be $\Gamma^0 = 0.8 \times 10^{-13}\ M\ cm^{-2}$. The standard potential, derived from the location of the curve on the potential axis, was found to be −1.097 V versus SCE. Upon addition of the acid, the whole $E_{1/2}$/log t curve shifts toward more positive values as the conversion of R^- to RH gets faster and faster. Simultaneously, the inflection disappears, whereas the long-time leveling off due to $R^{\bullet}$ dimerization remains. At high acid concentrations, the positive shift of the curve is less pronounced. It eventually stops when the conversion of $R^{\bullet}$ to R^- and RH is so fast that the forward electron transfer has become the rate-determining step. Before this limit is reached, simulation of the $E_{1/2}$/log t curves, using the previously determined values of E^0, k_S, k_d, k_0, Γ^0, provides the value of the protonation pseudo-first-order rate constant, k_1. The results are shown in Figure 2b. As expected, k_1 varies linearly with the acid concentration. The value of the second-order rate constant k is thus obtained from the slope of this diagram for the particular acid investigated in these experiments ($k = 9 \times 10^6\ M^{-1}\ s^{-1}$).

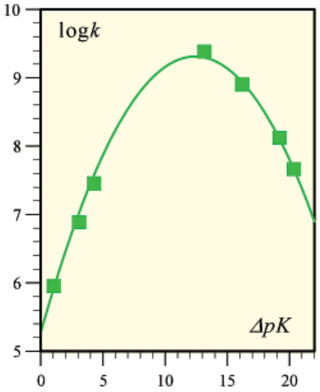

Figure 3. Protonation of the diphenylmethyl carbanion in DMF + 0.1 M Et_4NClO_4 at 22 °C. From left to right: water, methanol, benzhydrol, imidazole, benzyl mercaptan, acetic acid, benzoic acid; pK's are either taken from literature values[10a] or derived from the pK's in dimethyl sulfoxide (DMSO)[10b] according to $pK_{DMF} = 1.5 + 0.96 \times pK_{DMSO}$.[10a] In the case of benzhydrol, the pK in DMSO was derived from the pK in water[10c] according to the correlation $pK_{DMSO} = -2.9 + 2.1 \times pK_{water}$, being thus equal to 31.4, 30.5, 28.2, 19.35, 16.3, 13.3, 12.15. The pK of diphenylmethane derived from its value in DMSO[10b,c] is 32.4.

The same sort of experiments can be carried out with other acids. Figure 3 shows the results obtained with a series of seven "normal" acids[9] displayed under the form of a Brönsted plot relating the log of the protonation rate constant to the difference of pK between the acid and diphenylmethane over more than a 1 eV range of driving forces (repeated experiments showed that the precision on the rate constants is around 20%). Two features of this plot are worth mentioning. One is that the protonation exchange for this nonactivated carbon acid−base couple is intrinsically slow ($k = 10^5\ M^{-1}\ s^{-1}$), with an intrinsic barrier on the order of 1 eV. In this respect, it belongs to the same family as the activated carbon acid−base couples, in contrast with "normal" acid−base couples. The second remarkable feature is that there seems to be an inverted region in the Brönsted plot, reminiscent of what is predicted by the Marcus model of outersphere electron transfer. However, protonation reactions are not outersphere electron transfers, and more data should be gathered to confirm or infirm this preliminary observation and, more generally, to foster the establishment of a model of protonation exchange dynamics in nonactivated carbon acids. Examination of temperature dependences and investigation of other carbanions are in progress in this connection.

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(8) The transfer coefficient is assumed to be 0.5 in line with the fact that $E_{1/2}$ is not too distant from E^0.

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