Outer-Sphere Electron-Transfer Reduction of Alkyl Halides. A Source of Alkyl Radicals or of Carbanions? Reduction of Alkyl Radicals

**Claude P. Andrieux, Iluminada Gallardo,[1] and Jean-Michel Savéant***

Contribution from the Laboratoire d'Electrochimie Moléculaire de l'Université de Paris 7, Unité Associée au CNRS No. 438, 2 place Jussieu, 75251 Paris, Cedex 05, France. Received August 4, 1988

Abstract: Cyclic voltammetry of butyl iodides at an inert (glassy carbon) electrode allows the determination of an effective reduction potential for the *tert*- and *sec*-butyl radicals and of a lower limit of this quantity for the *n*-butyl radical. Taking into account the rapid self-reaction undergone by the radicals, a reduction potential (or, equivalently, the forward electron transfer rate constant) which is a combination of the standard potential and the intrinsic barrier of the $R^{\bullet}/R^{-}$ couple can be obtained. It provides all the necessary information for designing synthetic strategies based on the selective generation of either the radical or the carbanion from the electrochemical reduction of alkyl halides or of other radical-producing molecules. Modelling of the $R^{\bullet}/R^{-}$ kinetics by a quadratic activation–driving force relationship allows the determination of the intrinsic barriers and of the standard potentials. The latter were found to fall in the following ranges of values: *t*-Bu, 1.48, 1.60; *sec*-Bu, 1.38, 1.50; *n*-Bu, ≤−1.30, −1.42 V vs SCE.

The electrochemical reduction of monohaloalkanes has been the object of numerous investigations, mostly at mercury electrodes.[2] It, however, appears that mercury may be chemically involved in the reaction even in the cases where no stable organomercurials can be found in the reduction products. A mercury electrode should thus be considered as a heterogeneous inner sphere, rather than outer sphere, electron donor[3] in the reduction of alkyl halides. Glassy carbon, being much more chemically inert, is expected to be a suitable electrode material for outer-sphere electron transfer in the electrochemical reduction of alkyl halides. Cyclic voltammetry[4] and preparative scale reduction[4c,5] of several alkyl halides, mainly bromides and iodides,[6] at this electrode have been described.

Depending upon the nature of the halogen[6] and of the alkyl group (primary, secondary, tertiary), a single two-electron wave or a one-electron wave followed by a smaller wave has been observed in cyclic voltammetry.[5] The first or single waves are all irreversible, and it has been shown[4a,b,d] that the rate-determining step is, in all cases, the transfer of one electron concerted with the cleavage of the carbon-halogen bond, thus leading, in a first stage, to the alkyl radical:

$$RX + e^{-} \rightarrow R^{\bullet} + X^{-}$$
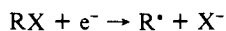
The alkyl radical thus formed may or may not be reduced by further transfer of one electron from the electrode at the potential where it has been formed. This is a quite important issue from a chemical viewpoint since the answer to the question should allow one to define the conditions under which either a radical or a

carbanion chemistry is opened up upon electrochemical reduction of alkyl halides at inert electrodes. The same is true for the homogeneous reduction of alkyl halides by outer-sphere electron donors such as, for example, aromatic anion radicals.[7] There are two other possible applications of the determination of the redox properties of the alkyl radical/carbanion couples. One is the estimation of the pK_a's of the corresponding hydrocarbons by means of appropriate thermodynamic cycles.[8] The other relates to the stabilities of low oxidation states of σ-alkyl metal complexes, an important issue in the design of organometallic catalytic cycles.[9] The difference in driving forces (DF) for the radical or carbanionic decomposition of such a complex:

$$M(n)R \rightarrow R^{\bullet} + M(n-1) \text{ vs } M(n)R \rightarrow R^{-} + M(n)^{+}$$
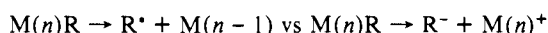
is indeed related to the standard potential of the $R^{\bullet}/R^{-}$ couple as[9]

$$DF(\text{radical}) - DF(\text{carbanionic}) = E^{\circ}{}_{[M(n)+/M(n-1)]} - E^{\circ}{}_{R^{\bullet}/R^{-}}$$

The work described hereafter is an attempt to derive the thermodynamic and kinetic characteristics of the reduction of alkyl radicals from the current–potential curves obtained for the re-

(1) Present address: Departamento Quimica-Fisica Facultad de Ciencias, Universidad Autonoma Barcelona, Bellaterra (Barcelona), Spain.
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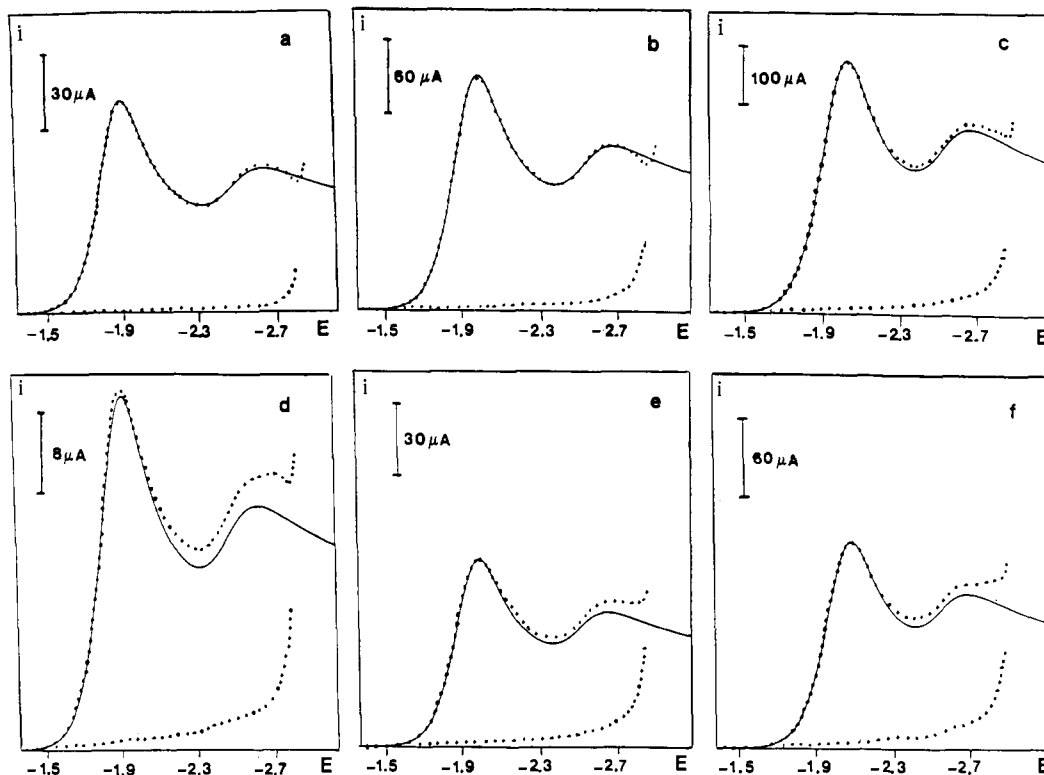(9) Gueutin, C.; Lexa, D.; Savéant, J-M.; Wang, D. L. *Organometallics*, in press.

Figure 1. Reduction of *t*-BuI at a glassy carbon electrode in DMF + 0.1 M Bu₄NBF₄: concn 5 (a–c) and 2 (d–f) mM; sweep rate; 0.2 (a, d), 1 (b, e), and 5 (c, f) V s⁻¹. The electrode potential E is expressed in volts and referred to the aqueous SCE: temp 10 °C; experimental (···) and simulated (—) curves.
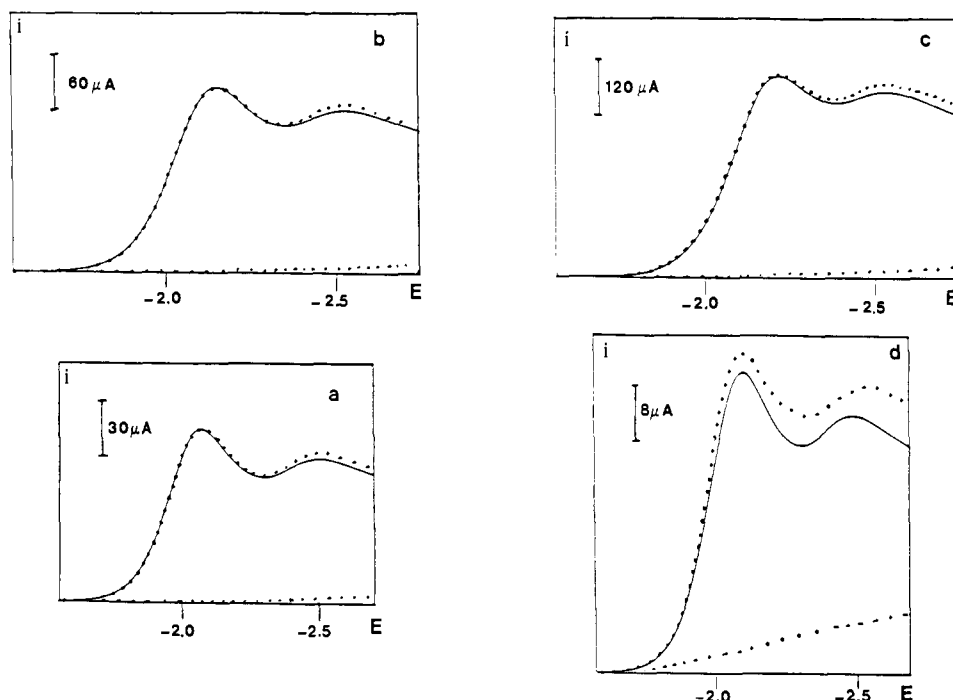

Figure 2. Reduction of *sec*-BuI at a glassy carbon electrode in DMF + 0.1 M Bu₄NBF₄: concn 5 (a–c) and 2 (d); sweep rate; 0.2 (a, d), 1 (b), and 5 (c) V s⁻¹; temp, 10 °C. The electrode potential E is expressed in volts and referred to the aqueous SCE.

duction of alkyl halides at an inert electrode (glassy carbon). The three butyl radicals were selected as illustrative examples, and the investigation was carried out with the corresponding iodides and bromides[6] in *N,N*-dimethylformamide (DMF).

Results and Discussion

The most interesting results, for our purpose, are those obtained with *t*-BuI (Figure 1) and *sec*-BuI (Figure 2) since the second wave that features the reduction of the alkyl radical is clearly separated from the first in the investigated potential range, thus

allowing an easy characterization of the reduction of the alkyl radical. The height of the first wave then corresponds to the transfer of one electron per molecule. With *t*-BuBr, a small second wave, overlapping the first wave, appears only at the lower edge of the accessible sweep rate range (Figure 3). With *sec*-BuBr, as well as with primary butyl iodide and bromide, a single two-electron irreversible wave is observed in the whole accessible sweep rate range. In the case of *t*- and *sec*-BuI, the first wave undergoes a large cathodic shift upon raising the sweep rate, of the order of 100 mV per decade, whereas the second wave is almost inde-
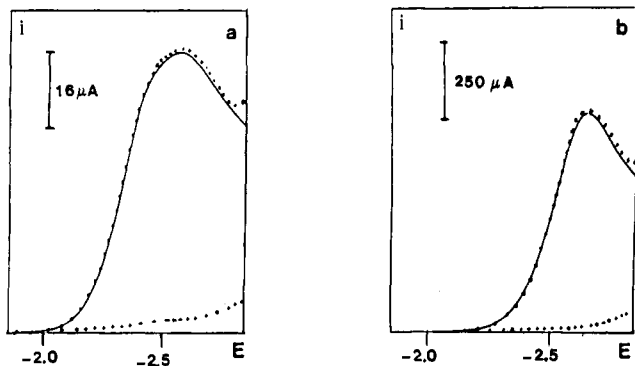
Figure 3. Reduction of *t*-BuBr at a glassy carbon electrode in DMF + 0.1 M NBu$_4$NBF$_4$: concn 5 mM; sweep rate, 0.05 (a), 5 (b); temp, 10 °C. The electrode potential *E* is expressed by volts and referred to the aqueous SCE.

pendent of this parameter. The alkyl halide concentration has no effect on the first wave, whereas the second wave undergoes a weak cathodic shift upon raising the concentration. We see the same trends with *t*-BuBr, but in this case a small increase in sweep rate suffices for obtaining a single two-electron wave (Figure 3). In all cases, the observation that the second wave has a much smaller height than that corresponding to one electron per molecule indicates that it does not feature the reduction of a stable product formed at the first wave but rather that of a transient species engaged in a homogeneous reaction,[10] the alkyl radical in the present case. Alkyl radicals undergo quite rapid bimolecular self-reactions, dimerization, and H-atom disproportionation, with a rate constant close to 5×10^9 M^{-1} s^{-1}.[11] These are presumably faster than H-atom abstraction from the solvent.[12] The latter is confirmed by the distribution of products (alkanes and alkenes) found in preparative-scale electrolysis of secondary and tertiary alkyl iodides at carbon electrodes in DMF.[4c]

The reduction process, as it appears, for example, in cyclic voltammetry, therefore corresponds to the following reaction scheme:

$$RX + e^- \rightarrow R^\bullet + X^- \tag{1}$$

$$R^\bullet + e^- \rightarrow R^- \tag{2}$$

$$2R^\bullet \xrightarrow{k} products \tag{3}$$
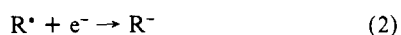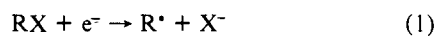
The carbanion, R$^-$, is rapidly consumed by reaction with proton donors present in the medium (residual water, quaternary ammonium cation of the supporting electrolyte, solvent) even if they are weak acids. Reactions 1 and 2 thus give rise to irreversible cyclic voltammetric waves. They both involve kinetic control by slow charge transfer. This is already known for reaction 1 which has been shown to proceed along a concerted electron transfer-bond breaking mechanism.[4a,b,d] Slow charge transfer is also heavily involved in the second wave, as will become clear in the following. Even if the activation driving force free energy relationships governing these two electron transfer reactions are nonlinear (most likely quadratic as discussed below), they can, with good accuracy, be linearized within the potential range where each of the waves appears and is not yet under diffusion control. In other words, the transfer coefficient, α, can be regarded as constant within this potential range.[13] In this context, the rate law governing each

of these electron transfer reactions can be formulated in a Butler-Volmer manner,[14] i.e., by the following relationship which has the same form for both RX and R$^\bullet$:

$$\frac{i}{FS} = k^f_{1,2} \exp\left(- \frac{\alpha_{1,2}FE}{RT} \right) C_{1,2} \tag{4}$$

where *S* is the electrode surface area; *E* is the electrode potential; i_1, i_2 are contributions to the total current, *i*, of the reduction of RX and R$^\bullet$, respectively; α_1, α_2 are respective transfer coefficients; k^f_1, k^f_2 are respective electron transfer forward rate constants referred to the reference electrode potential; and C_1 and C_2 are concentrations of RX and R$^\bullet$ at the electrode surface. As shown in the Experimental Section, the two-wave voltammograms can then be described, in dimensionless form, by the following coupled equations:

$$\Psi_1 = \exp(\alpha_1\xi)(1 - I\Psi_1) \tag{5}$$

$$\Psi_2 = \exp[\alpha_2(\xi - p)](\Psi_1 - \Psi_2)^{2/3} \tag{6}$$

where $I\Psi_1$ is the convolution integral:

$$I\Psi_1 = \frac{1}{\pi^{1/2}} \int_{-\infty}^{\xi} \frac{\Psi_1}{(\xi - \eta)^{1/2}} d\eta \tag{7}$$

The various dimensionless variables and parameters have the following meanings and definitions. Ψ_1 and Ψ_2 are dimensionless expressions of the currents i_1 and i_2, normalized toward a quantity representing a diffusion current:

$$\Psi_{1,2} = i_{1,2}/FSC^\circ(FvD/RT)^{1/2} \tag{8}$$

where C$^\circ$ is the bulk concentration of RX, v the sweep rate, and *D* the diffusion coefficient (assumed to be the same for RX and R$^\bullet$). ξ represents the electrode potential:

$$\xi = -(F/RT)(E - E^R_1) \tag{9}$$

referred to the "reduction potential" of RX itself defined as:

$$E^R_1 = \frac{RT}{\alpha_1 F} \ln\left[\frac{k^f_1}{(FvD/RT)^{1/2}} \right] \tag{10}$$

It is remarkable that within this formulation the dimensionless representation of the voltammograms depends, besides α_1 and α_2, only upon a single parameter:

$$p = \frac{F}{RT}(E^R_1 - E^R_2 + \Delta E^c) \tag{11}$$

where E^R_2 has the same definition as E^R_1 replacing α_1 and k^f_1 by α_2 and k^f_2, respectively, and:

$$\Delta E^c = \frac{RT}{3\alpha_2 F} \ln\left(\frac{RT4kC^\circ}{F3v} \right) \tag{12}$$

is a measure of the effect of the homogeneous reaction undergone by the alkyl radicals on the actual potential where their reduction takes place: the more difficult to reduce R$^\bullet$ as compared to RX, the more separated the waves. But the wave separation is also an increasing function of the rate of the bimolecular self-reaction of the alkyl radicals. Adjustable experimental parameters such

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(12) Russell, G. L. Reactivity, Selectivity and Polar Effects in Hydrogen Atom Transfer Reactions. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 7.

(13) Strictly speaking this is true only at one value of the sweep rate. Upon raising the sweep rate, the reduction potential becomes more negative, leading to an increase of the driving force of the reaction. If, then, the activation-driving force relationship is nonlinear, i.e., the transfer coefficient varies with the electrode potential, the transfer coefficient will vary with the sweep rate. This is more generally true for all parameters that control the location of the reduction potential, for example, the RX concentration in the case of the second wave. The present treatment of the effect of sweep rate and concentration will thus be only approximate, giving, however, a correct description of the general qualitative trends, in the case where the activation-driving force relationship is markedly nonlinear. This point will be further discussed in the following in the case of a quadratic activation-driving force relationship. It remains, however, that the approximation that α is a constant along the wave is perfectly valid since the range of potential where the wave is kinetically controlled by the electron transfer is rather narrow.

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Reduction of Alkyl Radicals

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Table I. Simulation of the Voltammograms obtained with *tert-* and *sec-*BuI. Derivation of the Reduction Characteristics of *tert-* and *sec-*Bu Radicals

concn v (V·s⁻¹)	*t*-BuI						*sec*-BuI			
	5 mM			2 mM			5 mM			2 mM
	0.2	1.0	5.0	0.2	1.0	5.0	0.2	1.0	5.0	0.2
E^P_1 [a,b]	−1.91	−1.97	−2.04	−1.91	−1.97	−2.04	−2.08	−2.15	−2.22	−2.08
α_1 [b]	0.31_7	0.30_8	0.29_7	0.31_7	0.30_8	0.29_7	0.31_5	0.30_6	0.29_5	0.31_5
E^R_1 [b]	-1.90_1	-1.96_6	-2.03_5	-1.90_{11}	-1.96_6	-2.03_5	-2.06_2	-2.13_4	-2.19_7	-2.06_2
$-\log k^f_1$ [c]	12.77	12.46	12.11	12.77	12.46	12.11	13.62	13.31	12.90	13.62
E^P_2 [a,b]	−2.62	−2.64	−2.66	−2.60	−2.61	−2.64	−2.50	−2.53	−2.54	−2.47
α_2	0.27_8	0.27_5	0.27_1	0.28_3	0.28_1	0.27_5	0.28_2	0.27_9	0.27_6	0.28_9
p	26.73	25.09	23.39	25.68	24.05	22.30	16.26	14.62	12.92	15.23
$E^R_2 - \Delta E^c$ [c]	-2.55_4	-2.57_9	-2.60_6	-2.52_9	-2.55_3	-2.57_9	-2.45_9	-2.49_1	-2.51_3	-2.43_4
ΔE^c [e]	0.44_5	0.40_3	0.36_1	0.41_2	0.36_8	0.32_8	0.43_9	0.39_7	0.35_4	0.42_2
E^R_2 [b]	-2.10_9	-2.17_5	-2.24_5	-2.11_7	-2.18_5	-2.25_1	-2.02_0	-2.09_4	-2.15_9	-2.03_2
$-\log k^f_2$ [c]	12.50	12.33	12.16	12.70	12.63	12.35	12.19	12.09	11.95	12.51
$\Delta G^*_{0,2}$ [d]	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58
$E°_2 + \Phi_r$ [b]	−1.59	−1.59	−1.60	−1.59	−1.59	−1.60	1.49	−1.50	−1.50	−1.49

[a] Cyclic voltammetric peak potential. [b] In V vs SCE. [c] k^f in cm s⁻¹. [d] In eV. [e] In V.

as sweep rate and initial RX concentration also appear in the expression of p: the larger the sweep rate and the smaller the concentration, the smaller the separation between the waves. In other words, the first wave undergoes a large negative shift ($28/\alpha_1$ mV per decade) as the sweep rate is raised, whereas the second wave shifts much less ($9/\alpha_2$ mV per decade) provided the two α's are not too different. The first wave thus catches up to the second, and the two waves eventually merge.[14] As to the effect of the RX concentration, it results from the fact that the first wave is independent of this factor, whereas the second wave shifts cathodically upon raising the concentration. The effect is, however, rather small ($19/\alpha_2$ mV per decade), much smaller than the effect of sweep rate. Figure 4 illustrates the variation of the dimensionless two-wave system as a function of p and thus of the various experimental parameters it contains. As seen in Figure 4, an increase in the parameter p has two effects. One is to increase the potential separation between the two waves. The other is to decrease the height of the second wave. In this connection, we note that, when the potential separation is big enough, the current corresponding to the reduction of R is never larger than that corresponding to the reduction of RX at the same potential and that the diffusion-controlled sections of the two curves, reached beyond the peak potential of the second wave, tend to merge.

The experimental results obviously fit in qualitatively with the foregoing analysis as far as the effects of sweep rate and concentration are concerned and also as to the differences in the behaviors of the investigated alkyl halides. Given the alkyl group, the two waves are more separated with the iodides than with the bromides because the reduction potential of the former is less negative than that of the latter.[15] Given the halogen, the separation of the waves increases in the order primary < secondary < tertiary indicating that their reduction potential becomes more and more negative in the same order as expected from inductive effects.

We can now go further and attempt to quantitatively simulate the experimental curves with the theoretical curves derived from the above equations. The results for *t*- and *sec*-BuI are shown in Figures 1 and 2. The best fit simulated curves correspond to the values of the parameters listed in Table I. In treating the data, D was taken as equal to 0.95×10^{-5} cm² s⁻¹.[16]

In the case of *t*-BuBr, we simulated the first wave with $\alpha_1 = 0.235$ and $\log k^f_1 = -12.38$ and introduce in the simulation the same values of α_2, k^f_2, and ΔE^c as previously obtained from the simulation of the *t*-BuI curves. A satisfactory fit of the experimental data is thus reached (Figure 3), confirming the validity

(15) This is essentially a consequence of the fact that the C–I bond is weaker than the C–Br bond, both of which make the standard potential of the reaction RX → R· + X⁻ more positive and decrease the standard activation free energy (intrinsic barrier).[4d]

(16) See ref 4a, noting the incidental inversion between the D and Z_{el} values for the iodide and bromides in Table V and the misprints in the second and third columns of the last line of the same table.
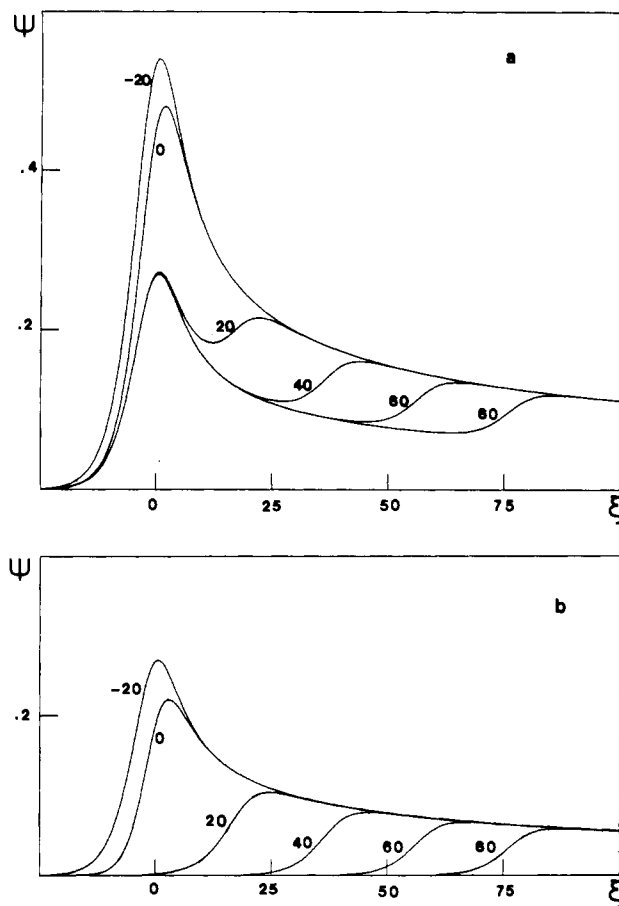

Figure 4. Variation of the dimensionless (eq 5 and 6) two-wave system with the parameter p (eq 11) for $\alpha_1 = 0.297$ and $\alpha_2 = 0.265$: (a) total current, (b) contribution of the reduction of R·. The numbers on the curves are the values of p.

of the α_2 and k^f_2 values obtained from *t*-BuI.

The reduction characteristics of *n*-Bu radicals cannot be reached in the same way since, even with the most easily reduced *n*-butyl halide, viz. *n*-BuI, a single two-electron wave is observed, even at the lowest accessible sweep rate. This can, however, provide an upper limit of the forward rate constant of electron transfer to the *n*-butyl radical. Simulation of the two-electron wave obtained with *n*-BuI at a concentration of 5 mM and a sweep rate of 0.1 V s⁻¹ gave $\alpha_1 = 0.30$ and $\log k^f_1 = -14.45$ ($E^R_1 = -2.30$). Assuming that α_2 is the same as for *t*- and *sec*-Bu, i.e., 0.28, we find that the merging of the two waves corresponds to $p = 3.63$, i.e., to $E^R_2 - \Delta E^c = -2.38$, thus to $E^R_2 = -1.92$ and to $\log k^f_2 = -11.78$.

We have thus come to an estimation of the transfer coefficient and of the forward rate constant of electron transfer to *tert*- and *sec*-butyl radicals and of an upper limit of the latter quantity for *n*-butyl radicals. The accuracy on these determinations is of the order of a few tens of millivolts in terms of potential, i.e., a factor of about 2 in terms of k^f_2.

From the values of α_2 and k^f_2 thus determined and from the rate constant of the homogeneous reaction undergone by the alkyl radicals, it is possible to predict their actual reduction potentials under any electrochemical conditions besides those of cyclic voltammetry.

Of particular interest in this connection is the case of preparative-scale reduction since the actual reduction potential then characterizes the transition between the triggering of a radical or a carbanion chemistry upon electrochemical reduction of alkyl halides or, more generally, of radical-producing substrates in which the X group is not necessary a halogen atom. Product distribution problems under preparative-scale steady-state conditions can be treated similarly to mechanistic problems in cyclic voltammetry.[17] With the present reaction scheme, the steady-state current potential curves are derived, in dimensionless form, from equations virtually identical with eq 5 and 6 (see Experimental Section):

$$\Psi_1 = \exp(\alpha_1\xi)(1 - \Psi_1) \qquad (13)$$

$$\Psi_2 = \exp[\alpha_2(\xi - p)](\Psi_1 - \Psi_2)^{2/3} \qquad (6)$$

in which the dimensionless currents, Ψ_1 and Ψ_2:

$$\Psi_{1,2} = i_{1,2}/i_L \qquad (14)$$

are now normalized toward a diffusion current, i_L, defined as:

$$i_L = FSC^\circ D/\delta \qquad (15)$$

where δ is the thickness of the steady-state diffusion layer. The expressions of ξ and p are the same as before, with now:

$$E^R_{1,2} = \frac{RT}{\alpha_{1,2}F} \ln\left(\frac{k^f_{1,2}\delta}{D}\right) \qquad (16)$$

and

$$\Delta E^c = \frac{RT}{\alpha_2 3F} \ln\left(\frac{4kC^\circ\delta^2}{3D}\right) \qquad (17)$$

for a bimolecular reaction and:

$$\Delta E^c = \frac{RT}{\alpha_2 2F} \ln\left(\frac{k\delta^2}{D}\right) \qquad (18)$$

for a first-order reaction. All the other symbols have the same meaning as before. In the cases where the reductions of RX and R• are well separated in potential, the half-wave potential of the R• wave, which represents the potential of transition between radical and carbanion chemistry, is thus (see Experimental Section):

$$E^t = E^R_2 - \Delta E^c + \frac{RT}{3\alpha_2 F} \ln 2 \qquad (19)$$

In usual preparative-scale conditions, δ is of the order of 10^{-2} cm and thus, for a bimolecular reaction of the alkyl radicals having the same rate constant as before and a 5 mM concentration,[18] the transition potential is predicted to be −2.47 (*t*-Bu), −2.38 (*sec*-Bu), >−2.30 (*n*-Bu), in V vs SCE.

These values can be readily adapted to the case where the radicals react with molecules present in the medium, rather than undergo self-reactions, by use of eq 18 instead of eq 17. The reduction potentials thus obtained can then be used to design synthetic strategies based on the selective generation of either radicals or carbanions by selection of the proper starting molecules and/or of the electrolysis potential. Note in this connection that,

in the current state of the art, it is easier to produce a carbanion from a molecule giving rise to a direct two-electron reduction than from a molecule showing two successive waves with the electrode potential set up at the second wave.[4c] This is due to the fact that ohmic drop varies during electrolysis making a willingly potentiostatic electrolysis actually galvanostatic in most cases. It should, however, be possible to overcome these problems by a proper design of the electrodes' geometry and a careful electronic control of the working electrode potential.

If we now want to split the information contained in the reduction potentials, E^R, into a standard potential, E°, and a standard activation free energy (intrinsic barrier), $\Delta G^\ddagger_0$, we need to know the form of the activation–driving force free energy relationship that governs the electron transfer reaction. That this is not quite linear appears in the experimental data gathered in Table I for both reactions 1 and 2; α slightly decreases as the sweep rate is raised in both cases and as the concentration is raised in the case of reaction 2. In other words, α decreases as the electrode potential is made more and more negative. The problem has been recently discussed for reaction 1, a concerted electron transfer–bond breaking process,[4a,b,d] and it has been shown that its kinetics can be satisfactorily modelled by a quadratic activation–driving force free energy relationship:[4d]

$$\Delta G^\ddagger = \Delta G^\ddagger_{0,1}\left(1 + \frac{E - E^0_1 - \Phi_r}{4\Delta G^\ddagger_{0,1}}\right)^2 \qquad (20)$$

($\Delta G^\ddagger$ is the activation free energy, E is the electrode potential, $\Delta G^\ddagger_{0,1}$ and E^0_1 are standard activation free energy and standard potential of the first electron transfer step, and r is the potential difference between the reaction site and the solution). No bond is broken during reaction 2 which can thus be regarded as an outer-sphere electron transfer, for which the same type of quadratic activation–driving force free energy relationship[19] applies:

$$\Delta G^\ddagger = \Delta G^\ddagger_{0,2}\left(1 + \frac{E - E^0_2 - \Phi_r}{4\Delta G^\ddagger_{0,2}}\right)^2 \qquad (21)$$

($\Delta G^\ddagger_{0,2}$ and E^0_2 are the standard activation free energy and standard potential of the second electron transfer step). As shown in the Experimental Section, $\Delta G^\ddagger_{0,2}$ and $E^0_2 + \Phi_r$ can be derived from the values of α_2, k^f_2, and E^p_2 previously determined (Table I) by means of the following relationships:

$$\Delta G^\ddagger_{0,2} = \frac{1}{4\alpha_2{}^2}\left(\frac{RT}{F} \ln \frac{Z^{el}}{k^f_2} + \alpha_2 E^p_2\right) \qquad (22)$$

$$E^\circ + \Phi_r = E^p_2 + 4\Delta G^\ddagger_{0,2}(1 - 2\alpha_2) \qquad (23)$$

Taking $Z^{el} = 4.6 \times 10^3$ cm s^{-1},[17] the values of $\Delta G^\ddagger_{0,2}$ and $E^0_2 + \Phi_r$ listed in Table I were found for the *tert*- and *sec*-butyl radicals. Practically the same value of $\Delta G^\ddagger_{0,2}$ is found for both radicals. We can thus take the same figure as a guessed value for the *n*-butyl radical and thus estimate that $E^0_2 + \Phi_r < -1.42$ V vs SCE in this case. As discussed earlier,[4a] the value of Φ_r can be estimated as being comprised between 0 and −0.12 V. The standard potentials of the $R•/R^-$ couple can thus be bracketed by the following figures (V vs SCE): *t*-Bu, −1.48, −1.60; *sec*-Bu, −1.38, −1.50; *n*-Bu, ≤−1.30, −1.42.

Note, however, that Φ_r is the same for the three radicals, thus allowing a meaningful comparison of one with the other. In this connection, since the value for *sec*-Bu is not very much positive

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(17) (a) See ref 17b,c and references cited therein. (b) Amatore, C.; Savéant, J-M. *J. Electroanal. Chem.* **1981**, *123*, 189. (c) Savéant, J-M. *J. Electroanal. Chem.* **1987**, *236*, 31.

(18) E^t shifts by −18 mV for a tenfold increase of RX concentration.

(19) (a) Experimental evidence of a quadratic activation–driving force free energy relationship,[19b–i] i.e., of a linear variation of with the electrode potential, has been provided for several organic molecule/anion radical couples (see ref 19j and references cited therein. (b) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962. (c) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (d) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966. (e) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (f) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (g) Waisman, E.; Worry, G.; Marcus, R. A. *J. Electroanal. Chem.* **1977**, *82*, 9. (h) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. (i) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265 in 245. (j) Savéant, J-M.; Tessier, D. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 57.

to that of *t*-Bu, the standard potential of *n*-Bu[*] should not be much positive to the indicated values. It should be emphasized that the values the standard potentials thus estimated are certainly much less precise than those of the reduction potentials determined above. They are indeed very sensitive to experimental uncertainty in the determination of α_2. From the degree of reproducibility of the cyclic voltammograms on the glassy carbon electrodes we used, it can be estimated that the resulting uncertainty on the determination of the standard potentials may reach 200 mV. It is, however, gratifying to find that *t*-Bu[*] is harder to reduce than *sec*-Bu[*], itself harder to reduce than *n*-Bu[*], as expected from electronic effects. This also falls in line with results obtained in the homogeneous reduction of alkyl halides by aromatic anion radicals[4] in which the reduction of the initially produced alkyl radical undergoes competitive electron transfer from and coupling with the aromatic anion radical. As a general trend, it has been shown that the coupling/reduction rate constant ratio decreases, for the same aromatic anion radical, in the order *t*-Bu > *sec*-Bu > *n*-Bu in keeping with the above order of standard potentials provided it is assumed that the coupling rate does not vary very much in the series.

Another remarkable feature of the above results is the slowness of electron transfer to simple alkyl radicals. It indeed has an intrinsic barrier as high as 0.58 eV. The main factors of nuclei reorganization occurring upon electron transfer are the solvent reorganization and the passage from a planar radical to a pyramidal carbanion. Solvent reorganization is certainly a major factor since the negative charge is highly concentrated on the central carbon in the carbanion ($\Delta G^{\ddagger}_0$ is approximately 0.5 eV for a 1 Å radius[20]).

Slowness of electron transfer to simple alkyl radicals makes their reduction potentials much more negative than their standard potentials. The recourse to a careful kinetic analysis of the reduction is thus necessary to estimate the standard potential. This is true whatever the method used to generate the radicals, for example, in the case of the elegant photoelectrochemical technique recently described and applied to benzyl-type radicals.[21] Another factor that affects the actual reduction potential measured from the electrochemistry of radical-producing molecules is the rapidity of the reactions, self-reactions or reactions with other molecules present in the medium, undergone by the radicals. Neglecting these two factors and thus taking the reduction potential as a measure of the standard potential may dramatically affect the estimation of other interesting thermodynamic quantities such as the pK_a of the corresponding alkanes.[8] As seen above, the standard potentials are about 1 V positive to the actual reduction potential which would result in an overestimation of the pK_a's of ca. 17 units (the pK_a of isobutane would thus be of the order of 54 rather than 71[8]).

Conclusions

Cyclic voltammetry of *tert*- and *sec*-butyl iodides at an inert (glassy carbon) electrode allows the determination of an effective reduction potential for the *tert*- and *sec*-butyl radicals. This is hardly possible with *tert*-butyl bromide and quite impossible with *sec*-butyl bromide since the reduction potential of the starting alkyl halide is then too negative for the reduction of the alkyl radical to appear. It is also the case with all *n*-butyl halides, including iodide, allowing only a lower limit for the reduction potential of *n*-butyl radical to be determined. These "effective reduction potentials" are functions of the standard potential and standard rate constant of the radical/carbanion couple as well as of the rate constant of the homogeneous reactions undergone by the radical. Knowing the latter, it is possible to derive the reduction potential or, equivalently, the forward electron transfer rate constant of the radical/carbanion couple. This quantity provides useful guidelines for synthetic strategies based on the selective

generation of either the alkyl radical or the alkyl carbanion. Close inspection of the kinetics of the electron transfer to butyl radicals shows that it can be modelled satisfactorily by a quadratic activation–driving force free energy relationship as many other organic redox couples. Estimates of both the standard potential and the standard activation free energy (intrinsic barrier) can thus be obtained. Electron transfer to butyl radicals thus appears as quite slow, involving intrinsic barriers of the order of 0.5–0.6 eV. This and the rapidity of the homogeneous reactions undergone by the butyl radicals make the actual reduction potentials that can be observed by any electrochemical technique much more negative (of the order of 1 V) than the corresponding standard potentials. This should be taken into account when deriving other interesting thermodynamic quantities, such as pK_a's of the corresponding hydrocarbons from the reduction potentials of alkyl radicals.

Experimental Section

The electrodes, cell and instrumentation as well as the various chemicals used were the same as previously described.[4a]

The procedures for treating the data were based on the following mathematical description and analysis of the electrochemical reduction of alkyl halides.

Calling a and b the concentrations of RX and R[*] normalized toward the bulk concentration of RX, R[*], the reduction of RX in cyclic voltammetry is described by the following set of partial derivative equations, initial and boundary conditions in the framework of linear and semiinfinite diffusion of the various intervening species to and from the electrode surface:

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \tag{24}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \lambda b^2 \tag{25}$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} \tag{26}$$

$$\tau = 0, y \geq 0 \text{ and } y = \infty, \tau \mid 0: \ a = 1, b = c = 0 \tag{27}$$

$$y = 0, \tau \geq 0: \ \partial a/\partial y + \partial b/\partial y + \partial c/\partial y = 0 \tag{28}$$

$$\partial a/\partial y = \Psi_1 = \exp(\alpha_1 \xi)a \tag{29}$$

$$-\partial c/\partial y = \Psi_2 = \exp[\alpha_2(\xi - \epsilon)]b \tag{30}$$

$\tau = Fvt/RT$ and $y = x/(FvD/RT)^{1/2}$ are dimensionless time and space variables, respectively (t = time; x = distance from the electrode surface). Ψ_1 and Ψ_2 are the dimensionless currents already defined in the text (eq 10). Note that $(\partial b/\partial y)_0 = \Psi_1 - \Psi_2$. Equations 24–26 describe the diffusion of RX, R[*], and R[-] to or from the electrode surface, modified in the case of R[*] by the term λb^2 representing the rate of the homogeneous bimolecular reactions undergone by the alkyl radicals (reaction 3). λ is thus a dimensionless expression of the homogeneous reaction rate constant:

$$\lambda = \frac{RT}{F} \frac{2kC^{\circ}}{v} \tag{31}$$

Equation 28 is a dimensionless formulation of the Butler–Volmer rate law for the reduction of RX as results from the definition of the dimensionless electrode potential in the text (eq 9 and 10). Equation 29 is likewise a dimensionless expression of the same kinetic law for the reduction of R[*]. Thus ϵ is the dimensionless expression of the difference between the reduction potentials of R[*] and RX (as defined in eq 10):

$$\epsilon = \frac{F}{RT}(E^R_1 - E^R_2) \tag{32}$$

Since reaction 3 is very rapid, $\partial b/\partial \tau = 0$ because of the steady state resulting from the mutual compensation of diffusion and homogeneous self-reactions of the alkyl radicals.[22] Integration of eq 25, taking eq 27, 28, and 30 into account, thus leads to:

$$\Psi_2 = (2\lambda/3)^{1/3} \exp[\alpha_2(\xi - \epsilon)](\Psi_1 - \Psi_2)^{2/3} \tag{33}$$

and thus to eq 6 with:

$$p = \epsilon + (1/3\alpha_2) \ln (2\lambda/3) \tag{34}$$

i.e., taking into account eq 31 and 32, to the same p as defined in the text by eq 11.

(20) See ref 4d and references cited therein.

(21) (a) Wayner, D. D. M.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 7764. (b) The intrinsic barrier for electron transfer may well be significantly lower with the benzyl-type radicals investigated in this study owing to possible charge delocalization on the phenyl ring.

On the other hand, integration of eq 24, taking eq 27 and 29 into account, classically[22] leads to eq 5, noting that ξ and τ are related by means of the linear relationship between the electrode potential and time, $E = E_i - vt$ (E_i = starting potential of the scan). Thus $\xi + u = \tau$, where $u = (F/RT)(E_i - E^R_1)$ is a dimensionless measure of the starting potential referred to the reduction potential E^R_1. In practice, $u = \infty$, meaning that the scan is started at a potential sufficiently positive to the waves for them to be independent of its exact value.

When going to preparative-scale conditions, eq 24–26 become ordinary differential equations since the time derivatives are now zero. Space is now normalized toward the thickness, δ, of the steady-state diffusion layer,[17,22] i.e., $y = x/\delta$. Accordingly, the currents are normalized toward the diffusion current i_1 (see eq 14 and 15 in the text). There are two sets of boundary conditions, one for the electrode surface ($y = 0$) which is formally the same as above (eq 28–30) and the other at the edge of the diffusion layer ($y = 1$) which is the same as eq 27. Integration, again taking into account the fact that, reaction 3 being rapid, $R^\bullet$ only exists in a thin reaction layer within the diffusion layer, immediately leads to eq 13 and 6. When the potential becomes more and more negative ($\xi \rightarrow \infty$), both Ψ_1 and $\Psi_2 \rightarrow 1$. The half-wave potential of the second wave, E^t, thus corresponds to $\Psi_2 = 0.5$. Application of eq 6 to this particular condition thus leads to eq 19.

In the linearization of the quadratic kinetic law:

$$\Delta G^\ddagger = \Delta G^\ddagger_0 \left(1 + \frac{E - E^0 - \Phi_r}{4\Delta G^\ddagger_0}\right)^2 \tag{35}$$

the transfer coefficient:

$$\alpha = \frac{1}{2}\left(1 + \frac{E - E^0 - \Phi_r}{4\Delta G^\ddagger_0}\right) \tag{36}$$

is regarded as constant and equal to its value at the peak:

$$\alpha = \frac{1}{2}\left(1 + \frac{E^P - E^0 - \Phi_r}{4\Delta G^\ddagger_0}\right) \tag{37}$$

Accordingly, the electrode potential is regarded as undergoing only small variations around the peak potential: $E = E^P + \Delta E$. Equation 35 can thus be linearized as:

$$\Delta G^\ddagger = \Delta G^\ddagger_0\left[\left(1 + \frac{E^P - E^0 - \Phi_r}{4\Delta G^\ddagger_0}\right)^2 + \frac{\Delta E}{2\Delta G^\ddagger_0}\left(1 + \frac{E^P - E^0 - \Phi_r}{4\Delta G^\ddagger_0}\right)\right] \tag{38}$$

i.e.,

$$\Delta G^\ddagger = 4\alpha(1 - \alpha)\Delta G^\ddagger_0 + \alpha(E - E^0 - \Phi_r) \tag{39}$$

Since

$$\Delta G^\ddagger = \frac{RT}{F}\ln\frac{Z^{el}}{k^f} + \alpha E \tag{40}$$

(Z^{el} is the heterogeneous collision frequency), it follows that:

$$\frac{RT}{F}\ln\frac{Z^{el}}{k^f} = 4\alpha(1 - \alpha)\Delta G^\ddagger_0 - \alpha(E^0 - \Phi_r) \tag{41}$$

The final equations used in the text (eq 22 and 23) then result from linear combination of eq 37 and 41.

(22) Andrieux, C. P.; Savéant, J-M. Electrochemical Reactions. In *Investigations of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Techniques of Chemistry; Wiley: New York, 1986; Vol. 6, 4/E. Part 2, pp 305–390.

Protonation Dynamics of [(C5H5)(CO)Fe]2(μ-CO)(μ-C=CH2) and Decomposition Processes for [(C5H5)(CO)Fe]2(μ-CO)(μ-C=CH2)H+ in the Gas Phase

D. B. Jacobson

Contribution from the Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105-5516. Received April 28, 1988

Abstract: The proton affinity (PA) and site of protonation of [(C5H5)(CO)Fe]2(μ-CO)(μ-C=CH2) (**2**), as well as the decomposition processes for [(C5H5)(CO)Fe]2(μ-CO)(μ-C=CH2)H+ (**7**), are studied in the gas phase by using Fourier transform mass spectrometry (FTMS). The PA of **2** is assigned as 232.5 ± 2 kcal/mol (relative to PA(NH3) = 204.0 kcal/mol) by using the bracketing technique. The site of protonation was determined by labeling studies to be the β-carbon of the μ-ethenylidene group of **2** yielding **3** in accord with the known solution chemistry. Protonation of **2** forming **3** implies that **3** is thermally more stable than isomeric μ-ethenyl species **6**. That both **3** and **6** have similar thermodynamic stability in solution implies that **6** is stabilized more by solvation than the corresponding μ-ethylidyne **3**. In contrast to solution, **3** is inert toward carbonyl electrophiles (aldehydes and ketones). This difference in reactivity, however, is consistent with the proposed reaction mechanism in solution involving initial protonation of the carbonyl species. The decomposition processes for collisionally activated **3** were studied in detail and compared with that for the non-protonated analogue [(C5H5)(CO)Fe]2(μ-CO)(μ-C=CH2)+ (**13**). **3** decomposes by initial elimination of the three carbonyls followed by sequential C2H2 and H2 eliminations yielding respectively [(C5H5)Fe]2H+ (**10**) and Fe2C10H9+. Hydrogen migration in the above fragment ions was investigated by monitoring H/D exchange with D2 and ethene-d4. No exchange occurs for any of the ions ([(C5H5)(CO)Fe]2(μ-CO)(μ-C=CH2)H+ through [(C5H5)Fe]2H+) with D2. With ethene-d4, one H/D exchange is observed with [(C5H5)Fe]2H+ (**10**), with *no* exchange for any of the larger fragment ions. Observation of only one exchange for **10** indicates that the exchangeable hydrogen is not scrambling with the cyclopentadienyl ring hydrogens.

Hydrocarbyl-bridged dinuclear transition-metal complexes[1] are the focus of increasing attention since they may serve as models for catalytic reactions. μ-Alkylidene and μ-alkylidyne dinuclear complexes are of particular interest due to their relevance as models for important catalytic processes including the Fischer–

Tropsch synthesis.[2] Cationic bridging alkylidyne–diiron complexes (**1**) have been the focus of recent studies owing to their ease of synthesis and thermal stability. Rosenblum and co-workers[3] first

(1) For a review see: Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135 and references cited therein.

(2) For reviews on Fischer-Tropsch synthesis, see: (a) Herrman, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Rofer-Depoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165.