

# Radical Ion Reactivity. III. A Theoretical Study of Proton Abstraction from Alkylaromatic Radical Cations, Based on Thermochemical Calculations

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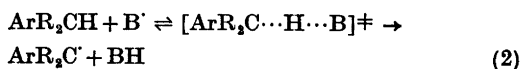
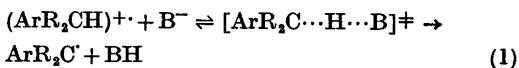
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Proton abstraction from the  $\alpha$  position of alkylaromatic radical cations has been treated theoretically, using a previously developed thermochemical method starting from the hypothesis that the transition state for reaction between a radical cation ( $\text{RH}^{\cdot+}$ ) and a base ( $\text{B}^-$ ) is identical to that for reaction between the corresponding neutral molecule ( $\text{RH}$ ) and radical ( $\text{B}^\cdot$ ). It is deduced that the proton abstraction process should be a very fast one, thus invalidating a number of previously postulated mechanisms for oxidative  $\alpha$  substitution of alkylaromatics *via* high-valence metal ions. As a further consequence the mechanism of other oxidative  $\alpha$  substitution reactions, *e.g.*, *via* high-potential quinones, are open for discussion since the existence of an isotope effect is not a definitive criterion for a rate-controlling proton transfer step. Finally, anodic acetoxylation in the presence of acetate ion again emerges as a suspected case of an indirect electrochemical mechanism, *i.e.*, anodically generated acetoxy radical attacks the substrate in a homolytic process.

We have previously shown<sup>1</sup> that radical cation reactivity *vs.* nucleophiles ( $\text{R}^{\cdot+}$  *vs.*  $\text{Nu}^-$ ) is to a large extent determined by the difference in standard potentials for the redox couples  $\text{R}^{\cdot+}/\text{R}$  and  $\text{Nu}^-/\text{Nu}^\cdot$ , respectively. This follows from the postulate that the transition state for reaction between  $\text{R}^{\cdot+}$  and  $\text{Nu}^-$  is identical to that for reaction between the corresponding neutral species,  $\text{R}$ , and radical,  $\text{Nu}^\cdot$ . Thermochemical calculations were performed for the *nuclear* attack of a series of nucleophiles upon four different radical cations, representing a

wide range of reactivity, and free energies of activation for these processes were worked out. In many cases testable predictions of both a quantitative and, perhaps more interesting, qualitative nature can be derived, making possible a critical examination of the usefulness of this postulate.

The same type of reasoning is applicable to *proton abstraction* from the  $\alpha$  position of alkylaromatic radical cations ( $\text{ArR}_2\text{CH}^{\cdot+}$ ) as was briefly discussed earlier<sup>2</sup> (see eqns. 1 and 2;  $\text{B}^-$  denotes a base). This paper presents



calculations of the energetics of eqn. 1 for a few typical radical cations and discusses critically known experimental data in the light of the derived thermochemical quantities.

## RESULTS

As for the  $\text{R}^{\cdot+}/\text{Nu}^-$  reaction,<sup>1</sup> the hypothesis that the transition states of eqns. 1 and 2 are identical leads to the conclusion that the free energy of activation of eqn. 1 ( $\Delta G^\ddagger_1$ ) should be obtained as the sum of the free energy of activation of eqn. 2 ( $\Delta G^\ddagger_2$ ) and the standard free energy difference ( $\Delta G^\circ_x$ ) between the initial states of the two reactions (see Fig. 1 in which  $\Delta G^\circ_x$  is assumed to be  $> 0$ ).

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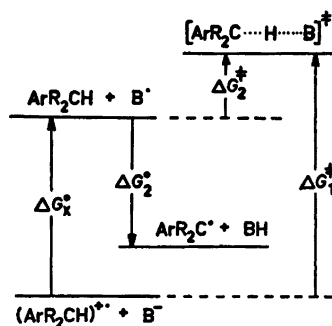
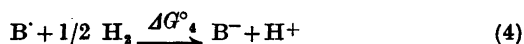
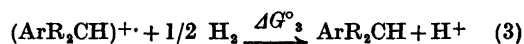


Fig. 1. Energy diagram showing the relationships between  $\Delta G^\circ_x$ ,  $\Delta G^\ddagger_1$  and  $\Delta G^\ddagger_2$  for the case that  $\Delta G^\circ_x > 0$ .

Values of  $\Delta G^\circ_x$  were obtained as the difference between the standard free energy changes of eqns. 3 and 4, which are seen to be related



to the standard potentials of the two redox couples,  $E^\circ_3$  and  $E^\circ_4$ , via the expression  $-\Delta G^\circ = 96.5 E^\circ$ . Calculations (see Table 1) were performed for  $E^\circ_3$  values of 2.6 V (corresponding to toluene), 2.0 V (durene) and 1.85 V [*p*-methoxytoluene (PMT) and hexamethylbenzene (HMB)] for the solvent/base systems most commonly encountered in the literature,<sup>3</sup> AcOH/AcO<sup>-</sup>, AcOH/H<sub>2</sub>O, trifluoroacetic acid/trifluoroacetate ion (TfacOH/TfacO<sup>-</sup>) and MeOH/MeO<sup>-</sup>. Since published  $E^\circ_4$  values refer to aqueous

solution,<sup>4</sup> corrections must be applied for the free energy of transfer of B<sup>•</sup> and B<sup>-</sup> from water to the solvent involved ( $\Delta G^\circ_{\text{B}^\bullet}$  and  $\Delta G^\circ_{\text{B}^-}$ ) according to eqn. 5. As before,<sup>1</sup>  $\Delta G^\circ_{\text{B}^\bullet}$  was simply put equal to zero.

$$\Delta G^\circ_x = 96.5 (E^\circ_4 - E^\circ_3) + \Delta G^\circ_{\text{B}^\bullet} - \Delta G^\circ_{\text{B}^-} \quad (5)$$

Unfortunately,  $\Delta G^\circ_{\text{B}^-}$  values for transfer from water to AcOH or TfacOH are not known but were approximated for both AcO<sup>-</sup> and TfacO<sup>-</sup> with  $\Delta G^\circ_{\text{AcO}^-}$  for transfer from water to formamide,<sup>5</sup> 16 kJ mol<sup>-1</sup>, in view of the similarity between these two ions.<sup>1</sup>

The standard potential of TfacO<sup>-</sup>/TfacO<sup>-</sup> was calculated as done previously for other carboxylates.<sup>4b</sup> The following thermodynamic quantities were used:  $\Delta H^\circ_f[\text{TfacOH}(1)]^\circ = -1069.0$  kJ mol<sup>-1</sup>, heat of solution of TfacOH in water assumed to be identical to that of AcOH<sup>7</sup> = -1.4 kJ mol<sup>-1</sup>, heat of neutralization of TfacOH<sup>8</sup> = 1.7 kJ mol<sup>-1</sup>,  $\Delta H^\circ_f[\text{TfacO}^\bullet(\text{aq})] = -824.2$  kJ mol<sup>-1</sup> (obtained from the estimated<sup>9</sup> value of  $\Delta H^\circ_f[(\text{TfacO})_2(\text{g})] = -1734.7$  kJ mol<sup>-1</sup>, based on an assumed heat of vaporization of liquid (TfacO)<sub>2</sub> equal to that of TfacOH = 39 kJ mol<sup>-1</sup>, and a *D*(O—O) value for (TfacO)<sub>2</sub> of 126 kJ mol<sup>-1</sup>; this latter value was calculated from known kinetic data for the decomposition of perfluoropropionyl peroxide<sup>10</sup> and is practically the same as *D*(O—O) for other simple diacyl peroxides<sup>11</sup>),  $S^\circ[\text{TfacO}^\bullet(\text{aq})] = 88$  and  $S^\circ[\text{TfacO}^\bullet(\text{aq})] = 181$  J K<sup>-1</sup> mol<sup>-1</sup> (the latter two values were taken to be equal to those of AcO<sup>-</sup> and AcO<sup>•4b</sup>). Using these data,  $E^\circ$  for TfacO<sup>-</sup>/TfacO<sup>-</sup> is calculated to be 2.0 V, ca 0.4 V lower than that of AcO<sup>-</sup>/AcO<sup>•4b</sup>.

Table 1.  $\Delta G^\circ_x$ ,  $\Delta G^\ddagger_2$ , and  $\Delta G^\ddagger_1$  values (kJ mol<sup>-1</sup>) for reaction between different solvent/base systems and the  $\alpha$  hydrogen of alkylaromatic radical cations (eqn. 1).

$E^\circ_3$	AcOH/AcO <sup>-</sup>			TfacOH/TfacO <sup>-</sup>			MeOH/MeO <sup>-</sup>			AcOH/H <sub>2</sub> O		
	$\Delta G^\circ_x$	$\Delta G^\ddagger_2$	$\Delta G^\ddagger_1$	$\Delta G^\circ_x$	$\Delta G^\ddagger_2$	$\Delta G^\ddagger_1$	$\Delta G^\circ_x$	$\Delta G^\ddagger_2$	$\Delta G^\ddagger_1$	$\Delta G^\circ_x$	$\Delta G^\ddagger_2$	$\Delta G^\ddagger_1$
2.6 <sup>a</sup>	-35	42	7	-75	48	-27	-84	54	-30	10	25	35
2.0 <sup>b</sup>	23	36	59	-17	45	28	-26	49	23	68	21	89
1.85 <sup>c</sup>	37	34	71	-2	43	41	-12	46	34	82	20	102

<sup>a</sup> Representing toluene, for which an  $E^\circ$  value of 2.61 V was determined<sup>7a</sup> in MeCN/(TfacO)<sub>2</sub>O (15:1)/Bu<sub>4</sub>NBF<sub>4</sub> (0.2 M) at -40°C. <sup>b</sup> Representing durene, for which an  $E^\circ$  value of 2.03 V was determined<sup>7a</sup> in MeCN/(TfacO)<sub>2</sub>O (15:1)/Bu<sub>4</sub>NBF<sub>4</sub> (0.2 M) at -40°C. <sup>c</sup> Representing *p*-methoxytoluene and hexamethylbenzene, for which  $E^\circ$  values of 1.82 and 1.85 V, respectively, were determined<sup>7a</sup> in MeCN/(TfacO)<sub>2</sub>O (15:1)/Bu<sub>4</sub>NBF<sub>4</sub> (0.2 M) at -40°C.

In order to calculate  $\Delta G^\circ_x$  for systems with  $B^- = H_2O$ ,  $E^\circ$  had to be estimated for the redox couple  $HO^\cdot + H^+/H_2O$  instead of  $H_2O^{\cdot+}/H_2O$ , since it turned out to be impossible to make any rational estimate of  $E^\circ$  for the latter system. There appears to be virtually nothing known about the stability and reactivity of  $H_2O^{\cdot+}$ , if it indeed has any existence at all in solution.  $E^\circ$  for  $HO^\cdot + H^+/H_2O$  was calculated to be 2.7 V from  $E^\circ$  of  $HO^\cdot/HO^-$  (1.9 V<sup>4a</sup>) and  $\Delta G^\circ$  of the water ionization process<sup>12</sup> (79 kJ mol<sup>-1</sup>).

$\Delta G^\ddagger_2$  values for attack of  $AcO^\cdot$  or  $TfacO^\cdot$  on an  $\alpha$  hydrogen of toluene are not known and no doubt will be exceedingly difficult to determine experimentally because of the extreme instability of these species toward decarboxylation.<sup>13</sup> An approximate rate constant for the abstraction of an allylic hydrogen by  $PhCOO^\cdot$  at 80 °C has, however, been determined<sup>14</sup> ( $2 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>) which gives  $E_a = 38$  kJ mol<sup>-1</sup>, assuming an  $A$  factor of  $10^{11}$  M<sup>-1</sup> s<sup>-1</sup> (corresponding to  $\Delta S^\ddagger = -56$  J K<sup>-1</sup> mol<sup>-1</sup>).  $D(PhCOO-H) = 427$  kJ mol<sup>-1</sup> is lower<sup>11</sup> than both  $D(AcO-H) = 469$  and  $D(TfacO-H) = 439$  kJ mol<sup>-1</sup> (obtained from the data given above) and hence it is reasonable to assume that  $AcO^\cdot$  and  $TfacO^\cdot$  are more reactive than  $PhCOO^\cdot$  in view of the well-known influence of the strength of the incipient bond upon hydrogen atom abstraction processes.<sup>15</sup> Thus  $\Delta G^\ddagger_2$  for attack of  $AcO^\cdot$  and  $TfacO^\cdot$  on an  $\alpha$  hydrogen of toluene (see Table 1) were based on an estimated increase in reactivity by a factor of 100 and 10, respectively, over that of  $PhCOO^\cdot$  and with the assumption that the reactivities of allylic and benzylic hydrogens are identical, entirely reasonable in view of the near-identity of  $D(CH_2=CHCH_2-H)$  and  $D(PhCH_2-H)$ .<sup>9</sup>

The rate constant for attack of methoxyl radical upon an  $\alpha$  hydrogen atom of toluene does not appear to be known so it had to be approximated as that of *t*-butoxyl radical,<sup>15,16</sup>  $6.3 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> at 40 °C, again assuming  $A = 10^{11}$  M<sup>-1</sup> s<sup>-1</sup> (*i.e.*  $\Delta S^\ddagger = -56$  J K<sup>-1</sup> mol<sup>-1</sup>).

The direct abstraction of an  $\alpha$  hydrogen in toluene by the hydroxyl radical takes place at a very high rate,<sup>17</sup>  $k$  being  $4 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> in aqueous solution at 25 °C; for other methylaromatic hydrocarbons the rate constant is practically the same, counted per methyl group. It is interesting to note that hydroxyl radical *adds* to the ring of these compounds

at an even faster rate,  $k$  being  $7 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for the whole series of methylbenzenes from toluene to HMB.<sup>17</sup>

For the remaining substrates of Table 1, except for the  $AcOH/H_2O$  system,  $\Delta G^\ddagger_2$  values were obtained by the same scale-down procedure as employed previously.<sup>1</sup>

## DISCUSSION

It should first be stressed that the estimates of  $\Delta G^\ddagger_1$  of Table 1 are subjected to considerable uncertainties due to the lack of relevant thermochemical and kinetic data for many of the key species and processes involved, as should already be obvious from the discussion above. In many cases the estimated values are based on analogies, approximations and mere guesswork and therefore considerable care must be exercised in the interpretation of  $\Delta G^\ddagger_1$  values. We are especially suspicious of the  $E^\circ$  value for  $TfacO^\cdot/TfacO^-$  since one key value,  $\Delta H^\circ_f[TfacO_2]$  is not an experimental one but instead calculated from known group contributions,<sup>9</sup> which in turn are partly derived from the heat of combustion of acetyl peroxide. Any destabilizing feature in trifluoroacetyl peroxide not present in acetyl peroxide would increase the  $E^\circ$  value. Since  $TfacO^-$  seems to be a lot more resistant toward anodic oxidation than  $AcO^-$  — as an example, anodic trifluoroacetylation in  $TfacOH/TfacO^-$  is possible for a number of deactivated aromatic compounds<sup>18,19</sup> which cannot be acetylated anodically in  $AcOH/AcO^-$  — one would intuitively expect its  $E^\circ$  value to be higher than that of  $AcO^\cdot/AcO^-$ , 2.41 V. On the other hand, resistance toward anodic oxidation may be due to kinetic inhibition<sup>20</sup> and thus give rise to the observed difference in anodic reactivity between  $TfacO^-$  and  $AcO^-$ . We have presently no way of deciding between these possibilities and therefore have to accept  $E^\circ = 2.0$  V for  $TfacO^\cdot/TfacO^-$ , although we cannot escape a feeling that it is somewhat too low.

The first prediction of interest that can be based upon the data of Table 1, is that the abstraction of a proton from  $ArR_2CH^+$  (eqn. 1) in the solvent/base systems treated should be a very fast to moderately fast process (with the possible exception of  $HMB^+/PMT^+$  in  $AcOH/H_2O$ ), as has indeed been tacitly as-

Table 2. Oxidative side-chain substitution reactions of toluene.

Solvent/base (additive)	Oxidant	Major products (relative yields)	Ref.
AcOH/AcO <sup>-</sup> Na <sup>+</sup>	Anode	PhCH <sub>2</sub> OAc(28), acetoxytoluenes (72, <i>o/m/p</i> = 43/11/46)	22
AcOH/AcO <sup>-</sup> K <sup>+</sup>	Anode	PhCH <sub>2</sub> Ac(23), acetoxytoluenes (77, <i>o/m/p</i> = 49/0/51)	23a
AcOH/NO <sub>3</sub> <sup>-</sup>	Anode	PhCHO(17), PhCH <sub>2</sub> OAc(46), PhCH <sub>2</sub> ONO <sub>2</sub> + PhCH <sub>2</sub> OH(33), PhCH <sub>2</sub> CH <sub>2</sub> Ph(4)	23b
AcOH/NO <sub>3</sub> <sup>-</sup>	Anode	PhCHO(13), PhCH <sub>2</sub> OAc(39), PhCH <sub>2</sub> ONO <sub>2</sub> (27), PhCH <sub>2</sub> CH <sub>2</sub> Ph(3), acetoxytoluenes(9, <i>o/p</i> = 1.6)	23a
AcOH/AcOH (TsO <sup>-</sup> )	Anode	PhCHO(12), PhCH <sub>2</sub> OAc(47), PhCH <sub>2</sub> CH <sub>2</sub> Ph(31)	23a
AcOH/AcOH (BF <sub>4</sub> <sup>-</sup> )	Anode	PhCH <sub>2</sub> OAc(100)	24
TfacOH-Me <sub>2</sub> CO/ TfacO <sup>-</sup>	Anode	PhCH <sub>2</sub> OTfac(50), MeC <sub>6</sub> H <sub>4</sub> OTfac(50, <i>o/m/p</i> = 51/5/44)	25
AcOH/AcO <sup>-</sup>	Co(III)	PhCHO(12), PhCH <sub>2</sub> OAc(78), dehydrodimers (7)	26
AcOH/AcO <sup>-</sup> (LiCl)	Co(III)	PhCHO(4), PhCH <sub>2</sub> OAc(5), PhCH <sub>2</sub> Cl(84), ClC <sub>6</sub> H <sub>4</sub> Me(7)	26
TfacOH/TfacO <sup>-</sup>	Co(III)	PhCH <sub>2</sub> OTfac(67), dehydrodimers(33)	27
TfacOH/TfacO <sup>-</sup> (LiCl)	Co(III)	PhCH <sub>2</sub> Cl (< 5), dehydrodimer + trimer(67), ClC <sub>6</sub> H <sub>4</sub> Me (28, <i>o/p</i> = 41/59)	28
MeCN/H <sub>2</sub> O (HClO <sub>4</sub> )	Co(III)	PhCHO(61), PhCH <sub>2</sub> CH <sub>2</sub> Ph(0.5), PhCH <sub>2</sub> OH(9), PhCOOH(29)	34
AcOH/H <sub>2</sub> O	[Co(III)O <sub>4</sub> W <sub>12</sub> O <sub>36</sub> ] <sup>5-</sup>	PhCH <sub>2</sub> OAc	29
AcOH/AcO <sup>-</sup>	Pb(IV)	PhCHO, PhCH <sub>2</sub> OAc	30
AcOH-TfacOH(91:9)/ TfacO <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup> /Cu(II)	PhCH <sub>2</sub> OTfac, PhCH <sub>2</sub> OAc	31
H <sub>2</sub> O/SO <sub>4</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup> /Cu(II)	PhCH <sub>2</sub> OH(42), HOC <sub>6</sub> H <sub>4</sub> Me(58, <i>o/m/p</i> = 62/5/33)	32
H <sub>2</sub> O/SO <sub>4</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup> /Fe(III)	PhCHO(4), PhCH <sub>2</sub> OH(21), PhCH <sub>2</sub> CH <sub>2</sub> Ph(53), HOC <sub>6</sub> H <sub>4</sub> Me(22, <i>o/m/p</i> = 57/2/41)	33

Table 3. Oxidative side-chain substitution reactions of durene (in this table denoted either ArCH<sub>2</sub> or Ar'H).

Solvent/base (additive)	Oxidant	Major products (relative yields)	Ref.
AcOH/AcO <sup>-</sup>	Anode	ArCH <sub>2</sub> OAc(100)	24a
AcOH/AcOH (BF <sub>4</sub> <sup>-</sup> )	Anode	ArCHO(6), ArCH <sub>2</sub> OAc(91), ArCH <sub>2</sub> Ar'(3)	24b
MeCN/H <sub>2</sub> O (BF <sub>4</sub> <sup>-</sup> )	Anode	ArCHO(6), ArCH <sub>2</sub> NHOAc(68), ArCH <sub>2</sub> Ar'(26)	35
MeCN-TfacOH (BF <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> Ar'(100)	36
MeCN-CF <sub>3</sub> SO <sub>3</sub> H (BF <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> Ar'(100)	36
CH <sub>2</sub> Cl <sub>2</sub> (BF <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> Ar', Ar'CH <sub>2</sub> Ar'	37
TfacOH-CH <sub>2</sub> Cl <sub>2</sub> / TfacO <sup>-</sup>	Co(III)	ArCH <sub>2</sub> Ar(29), ArCH <sub>2</sub> Ar'(51), 1,2,4,5,6,8-Me <sub>6</sub> -anthracene(20)	38
TfacOH-CH <sub>2</sub> Cl <sub>2</sub> / TfacO <sup>-</sup>	Mn(III)	ArCH <sub>2</sub> Ar(23), ArCH <sub>2</sub> Ar'(26), 1,2,4,5,6,8-Me <sub>6</sub> -anthracene(51)	38
CH <sub>2</sub> Cl <sub>2</sub> /Cl <sup>-</sup>	Fe(III)	ArCH <sub>2</sub> Ar(18), ArCH <sub>2</sub> Ar'(82)	39

sumed for a long time<sup>3</sup> and recently also demonstrated by spectroelectrochemical methods<sup>21</sup> in the anodic oxidation of some of the substrates discussed here (for lists of oxidative  $\alpha$  substitution reactions of toluene, durene, PMT and HMB, see Tables 2-5). Rate constants for

such reactions are, however, scarce in the literature up till now, being largely limited to those determined very recently by pulse radiolytic studies in aqueous solution;<sup>53,54</sup> only one electrochemically determined rate constant seems to have been reported.<sup>51b</sup> These data

Table 4. Oxidative side-chain substitution reactions of *p*-methoxytoluene (in this table denoted either ArCH<sub>3</sub> or Ar'H).

Solvent/base (additive)	Oxidant	Major products (relative yields)	Ref.
AcOH/AcO <sup>-</sup>	Anode	ArCH <sub>2</sub> OAc(99), Ar'OAc(1)	22
MeCN/H <sub>2</sub> O (ClO <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> NHAc(100)	40
MeOH/MeO <sup>-</sup>	Anode	ArCH <sub>2</sub> OMe(27), ArCH(OMe) <sub>2</sub> (28), 3,3,6-trimethoxy-6-methylcyclohexadiene <sup>a</sup> (45)	41
MeOH/CN <sup>-b</sup>	Anode	Ar'CN(35), ArCH <sub>2</sub> CN(trace), ArCH <sub>2</sub> OMe(22), ArCH(OMe) <sub>2</sub> (44)	42
AcOH/AcO <sup>-</sup> (LiCl)	Co(III)	ArCHO(4), ArCH <sub>2</sub> Cl + ArCH <sub>2</sub> OAc(96)	26
AcOH/AcO <sup>-</sup>	Mn(III)	ArCHO(10), ArCH <sub>2</sub> OAc(90)	45
AcOH/AcO <sup>-</sup> (Ac <sub>2</sub> O)	Mn(III)	ArCHO(1), ArCH <sub>2</sub> OAc(99)	22
AcOH/AcO <sup>-</sup> (H <sub>2</sub> O)	Mn(III)	ArCHO(10), ArCH <sub>2</sub> OAc(90)	22
AcOH/AcO <sup>-</sup> (2,2'-bipyridine)	Ag(II)	ArCHO(23), ArCH <sub>2</sub> OAc(77)	46

<sup>a</sup> Product of nuclear attack. <sup>b</sup> Cyanide ion exists in equilibrium with methoxide ion in methanol in a ratio of ca. 24:1.<sup>43</sup> Neither in dichloromethane/CN<sup>-</sup> is side-chain cyanation observed.<sup>44</sup>

Table 5. Oxidative side-chain substitution reactions of hexamethylbenzene (in this table denoted ArCH<sub>3</sub>).

Solvent/base (additive)	Oxidant	Major products (relative yields)	Ref.
AcOH/AcO <sup>-</sup>	Anode	ArCH <sub>2</sub> OAc(100)	24a
AcOH/AcOH (BF <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> OAc(100)	24b
TfacOH/(BF <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> OTfac(100)	47
TfacOH-CH <sub>2</sub> Cl <sub>2</sub> (1:9)/(BF <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> OTfac(100)	48
TfacOH-CH <sub>2</sub> Cl <sub>2</sub> (1:9)-mesitylene (2.5 M)/(BF <sub>4</sub> <sup>-</sup> )	Anode	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> Ar(87), ArH(5), (2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> (8)	48
MeCN/H <sub>2</sub> O (BF <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> NHAc(100)	21,49
MeCN/H <sub>2</sub> O (ClO <sub>4</sub> <sup>-</sup> )	Anode	ArCH <sub>2</sub> NHAc(100)	35,50
MeCN/H <sub>2</sub> F <sub>4</sub> <sup>-</sup>	Anode	ArCH <sub>2</sub> F(88), ArCH <sub>2</sub> NHAc(12)	51
AcOH/AcO <sup>-</sup> (2,2'-bipyridine)	Ag(II)	ArCH <sub>2</sub> OAc(76), ArCH <sub>2</sub> OH(24)	46
AcOH/NO <sub>3</sub> <sup>-</sup>	Ce(IV)	ArCH <sub>2</sub> ONO <sub>2</sub> , ArCH <sub>2</sub> OAc (ratio > 1.4)	52
AcOH/Tfac (91:9)	SO <sub>4</sub> <sup>2-</sup>	ArCH <sub>2</sub> OTfac + ArCH <sub>2</sub> OAc	31

have been collected in Table 6. From the few comparisons between estimated and experimental values that are possible, it is seen that too low rates are predicted by our method, except for PhCH<sub>3</sub><sup>+</sup>. In view of the approximations involved in the calculations both absolute values and trends are reproduced reasonably well at the present state of knowledge, and we expect that future experimentation will make possible considerably more stringent tests of our starting hypothesis and its consequences. In the meantime it is of interest to pursue a

few lines of thought concerning proton abstraction from radical cations, since the mere realization and demonstration that it is a fast reaction is bound to force us to undertake mechanistic revisions in a number of cases.

An interesting problem is connected with oxidative  $\alpha$  substitution in which a high valence metal ion acts as the oxidant.<sup>3d</sup> After the penetrating mechanistic study by Andrusis *et al.*<sup>45</sup> such reactions have generally been thought of as involving a fast and reversible initial electron transfer step, followed by a slow proton ab-

Table 6. Reported rate constants for proton abstraction from alkylaromatic radical cations. Data were taken from Ref. 53 unless otherwise indicated.

Radical cation derived from	Solvent/base	Rate constant/10 <sup>3</sup> M <sup>-1</sup> s <sup>-1</sup>	$\Delta G^\ddagger$ ,/kJ mol <sup>-1</sup> Experimental	Estimate (Table 1)
Toluene	H <sub>2</sub> O/H <sub>2</sub> O	1800	44	35
<i>o</i> -Xylene	H <sub>2</sub> O/H <sub>2</sub> O	360		
<i>m</i> -Xylene	H <sub>2</sub> O/H <sub>2</sub> O	360		
<i>p</i> -Xylene	H <sub>2</sub> O/H <sub>2</sub> O	250		
1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	H <sub>2</sub> O/H <sub>2</sub> O	270		
1,2,3-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	H <sub>2</sub> O/H <sub>2</sub> O	270		
1,2,4-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	H <sub>2</sub> O/H <sub>2</sub> O	360		
1,2,3,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub> O	18	55	89 <sup>a</sup>
1,2,3,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	H <sub>2</sub> O/AcO <sup>-</sup>	50 000 <sup>44</sup>	36	59 <sup>a</sup>
1,2,3,4-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub> O	45		
1,2,4,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub> O	5	58	89
Me <sub>5</sub> C <sub>6</sub> H	H <sub>2</sub> O/H <sub>2</sub> O	2.8		
Me <sub>5</sub> C <sub>6</sub> H	MeCN/H <sub>2</sub> O	0.14 <sup>21 b</sup>		
Me <sub>6</sub> C <sub>6</sub>	H <sub>2</sub> O/H <sub>2</sub> O	1 <sup>b</sup>	62	102

<sup>a</sup> Assuming  $E^\circ$  for isodurene equal to that of durene ( $E_{1/2}$  values are 1.43 and 1.29 V vs. Ag/0.1 M Ag<sup>+</sup>, respectively<sup>55</sup>). <sup>b</sup> Estimated value.

straction step (eqns. 6 and 7). Both kinetic arguments and the existence of a large kinetic deuterium isotope effect supported this mechanism, generally assumed to be valid for ions such as Co(III),<sup>26,27</sup> Mn(III),<sup>45</sup> Ag(II)<sup>46</sup> and



Ce(IV)<sup>25</sup> whereas for Pb(IV),<sup>30</sup> Cr(VI),<sup>56,57</sup> and Pd(II)<sup>58</sup> other types of mechanisms, involving

hydrogen transfer to the metal center, have been proposed in the majority of cases.<sup>3d</sup>

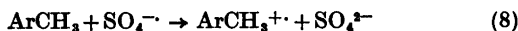
Table 7 lists  $k_{\text{H}}/k_{\text{D}}$  for a number of oxidative  $\alpha$  substitution processes and we see that most of the metal ion promoted processes exhibit large isotope effects. In view of the high rates of the proton abstraction reaction (Table 6) and the fairly low overall rates of most of the reactions in Table 7 it is, however, in some cases untenable to maintain that the mechanism represented by eqns. 6 and 7 can be valid. Instead it is obvious that both electron transfer

Table 7. Primary kinetic deuterium isotope effects in oxidative side-chain substitution of alkylaromatic compounds.

Oxidant	Solvent/base	Substrate	$k_{\text{H}}/k_{\text{D}}$ (Temp./°C)	Ref.
Anode	AcOH/AcO <sup>-</sup>	PhEt	2.6 (25)	22
Co(III)	AcOH/AcO <sup>-</sup>	PhMe	3.7 (24)	26
Co(III)	AcOH-TfacOH/TfacO <sup>-</sup>	PhMe	1.1 (20)	27
Mn(III)	AcOH/AcO <sup>-</sup>	4-MeOC <sub>6</sub> H <sub>4</sub> Me	4.8 (70)	45
Ag(II)	AcOH/AcO <sup>-</sup>	4-MeOC <sub>6</sub> H <sub>4</sub> Me	5.9 (25)	46
Ce(IV)	AcOH/NO <sub>3</sub> <sup>-</sup> ?	PhMe	1.8	52
Pb(IV)	HF (liq)/HF <sub>2</sub> <sup>-</sup>	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Me	4.8 (0)	59
Cr(VI)	AcOH-H <sub>2</sub> O-HClO <sub>4</sub> /H <sub>2</sub> O	Cycloheptatriene	1.0 (30)	56
Cr(VI)	AcOH-H <sub>2</sub> O-HClO <sub>4</sub> /H <sub>2</sub> O	Ph <sub>2</sub> CH <sub>2</sub>	5.0 (30)	57
Tetrachloro- <i>p</i> -quinone	MeCN	(4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> CH	10 (15)	60
2,3-Dichloro-5,6-dicyano- <i>p</i> -quinone (DDQ)	AcOH	Cycloheptatriene	4.0 (25)	61
DDQ	AcOH/AcOH	4-MeOC <sub>6</sub> H <sub>4</sub> Me	3.7 (110)	62
SO <sub>4</sub> <sup>-</sup>	AcOH/AcO <sup>-</sup>	PhMe	2.2 (110)	31
dP(II)	AcOH/AcO <sup>-</sup>	PhCH <sub>3</sub>	4.0 (110)	58

and proton transfer somehow must be involved in the rate-determining step, perhaps in a concerted fashion, as was proposed for, *e.g.*, Co(III) oxidation of alkylarenes already some ten years ago,<sup>34</sup> and very recently in a different context, autoreduction of tetraphenylporphyrinatoiron(III) chloride in the presence of piperidine,<sup>53a</sup> for which the intramolecular electron transfer between Fe(III) and a coordinated piperidine is facilitated by the deprotonation of the coordinated piperidine by free piperidine ( $k_H/k_D \approx 2$ ). Also direct hydrogen atom abstraction by the metal center has been suggested earlier<sup>3d</sup> for certain ions [Co(III), Pb(IV), Cr(VI) and Mn(III)] and will probably have to be considered in the future for the other metal ions listed in Table 7.

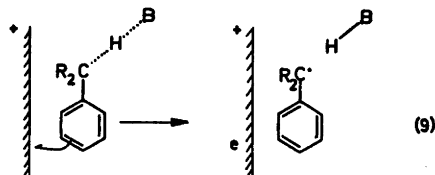
It should be pointed out that some of the processes listed in Table 7 *might* follow a mechanism with a slow proton transfer step (eqns. 6 and 7), depending upon the oxidizing power of the reagent and hence the rate of the electron transfer step. Thus, sulfate radical ( $\text{SO}_4^{\cdot-}$ ) has been shown<sup>53b</sup> by pulse radiolysis experiments to give radical cations of methylbenzenes by electron transfer oxidation in aqueous solution (eqn. 8) with rate constants of  $(1-2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This step is entirely reasonable in view



of the very high  $E^\circ$  value of  $\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}$  in water, 2.6 V, which means that the rate of electron transfer must be diffusion controlled. With  $k$  for proton abstraction at least four powers of ten smaller (Table 6) we have an authentic case of the mechanism given by eqns. 6 and 7, at least in aqueous solution. The  $k_H/k_D$  value given in Table 7, 2.2 at 110 °C in acetic acid,<sup>31</sup> is not unreasonable for this mechanism but of course one cannot be sure that the kinetic relationships in this solvent are the same as in water.

Likewise, the reaction between Ag(II) and aromatic compounds in aqueous solution is known to be a fast process ( $k \text{ ca. } 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for a series of substrates<sup>63</sup>) compared to proton abstraction, so that also here the sequence of eqns. 6 and 7 constitutes a viable mechanism. Again, in Ag(II) mediated acetoxylation in acetic acid<sup>46</sup> we observe an isotope effect ( $k_H/k_D = 5.9$  at 25 °C) but cannot be sure that the kinetic relationships are the same as in water.

Finally, anodic acetoxylation in which the radical cation is generated in a heterogeneous electron transfer step,<sup>22</sup> is not wholly compatible with the other reactions; here the isotope effect might either originate from the proton transfer step of eqn. 7, hydrogen atom abstraction by  $\text{Me}^\cdot$  or  $\text{MeCOO}^\cdot$  (see below), or from a step involving synchronous electron/proton transfer from a substrate molecule adsorbed at the electrode (eqn. 9), as advocated earlier.<sup>22</sup>



The anodic cyanation of aromatic compounds has been investigated in  $\text{MeOH}/\text{CN}^-$ ,  $\text{MeCN}/\text{CN}^-$  and/or  $\text{CH}_2\text{Cl}_2/\text{CN}^-$  in a large number of cases,<sup>42,43,64</sup> nuclear substitution being the most commonly observed process (1,4-addition of two cyano groups or one cyano and one methoxy group across the aromatic ring has also been found in some instances<sup>65</sup>). It is, however, not possible to find any recorded case of  $\alpha$  cyanation, except possibly one; PMT, for which  $\alpha$  substitution should be especially favored, was reported<sup>42</sup> to give trace amounts of *p*-methoxybenzyl cyanide besides large amounts of nuclear cyanation products on anodic oxidation in  $\text{MeOH}/\text{CN}^-$ . In  $\text{CH}_2\text{Cl}_2/\text{CN}^-$ , where the generally higher reactivity of cyanide ion<sup>65</sup> would be expected to enhance its basicity, no  $\alpha$  cyanation product was, however, detectable from the anodic oxidation of PMT.<sup>44</sup> Why is it then that cyanide ion, a relatively strong base, does not abstract a proton from  $\text{PMT}^{\cdot+}$  or any other suitable substrate? According to calculations (see Table 1 under  $\text{MeOH}/\text{MeO}^-$ ; the system  $\text{MeO}^\cdot/\text{MeO}^-$  has very nearly the same  $E^\circ$  value as  $\text{CN}^\cdot/\text{CN}^-$ , whereas  $\Delta G^\ddagger_2$  values should be somewhat lower) this process should be very fast and certainly able to compete favorably with nuclear attack by  $\text{CN}^-$  upon  $\text{PMT}^{\cdot+}$  for which approximately the same rate constant can be estimated.

At present it is not easy to suggest a reasonable mechanism which can explain the extremely low  $\alpha$ /nuclear substitution ratio in anodic cyanation (much lower than for acetox-

ylation). We have however for other reasons previously concluded<sup>1</sup> that anodic nuclear cyanation should take place *via* spin density controlled coupling between simultaneously generated cyano radicals and radical cations and tentatively suggest that this mechanism opens a possible way out of the difficulties with the mechanism of eqn. 1. For any  $\text{ArCH}_3^+$  with a reasonably high  $E^\circ$  value (above  $\sim 1.7$  V) an encounter with  $\text{CN}^-$  leads to electron transfer (and not proton transfer or nuclear attack) between the two species. Hence  $\alpha$  substitution can only occur as a result of attack by  $\text{CN}^-$  upon an  $\alpha$  hydrogen of  $\text{ArCH}_3^+$  or  $\text{ArCH}_3$  and it may be that these reactions are considerably slower than the coupling process leading to nuclear substitution (which should be diffusion controlled). A corollary of this proposal would be that an  $\text{ArCH}_3^+$  with a sufficiently low  $E^\circ$  (say,  $\leq 1.0$  V) might undergo proton abstraction (and not electron transfer reduction) by cyanide ion and hence give an  $\alpha$  cyano substitution product. It does not seem impossible to find such a system.

It is not altogether obvious that methoxylation should differ from cyanation with respect to the tendency for  $\alpha$  substitution; methoxide ion is an easily oxidizable species and in fact so similar to cyanide ion in its redox properties that it would be expected to behave similarly. Yet anodic side-chain methoxylation is observed to be the predominant reaction for PMT, at least at a carbon electrode (Table 4).

Another puzzling problem in oxidative acyloxylation concerns the role of the carboxylate ion in determining the ratio between  $\alpha$  and nuclear substitution, a situation that now can be analyzed somewhat more in detail. For the anodic oxidation of alkylbenzenes it was early observed<sup>22,23b</sup> that the presence of acetate ion in the electrolyte was necessary for nuclear acetoxylation to occur at all, whereas the use of salts of non-nucleophilic anions (such as perchlorate, tetrafluoroborate, tosylate, *etc.*) changes site of attack to exclusively the  $\alpha$  position. Assuming that water or acetic acid is the base in the latter case we see from the calculations of Table 1 that the opposite behaviour is predicted, *i.e.* acetate ion should be far more effective than water or acetic acid in abstracting a proton from  $\text{ArCH}_3^+$ , as is indeed borne out by kinetic measurements (Table

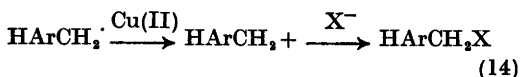
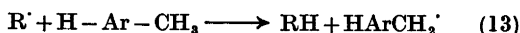
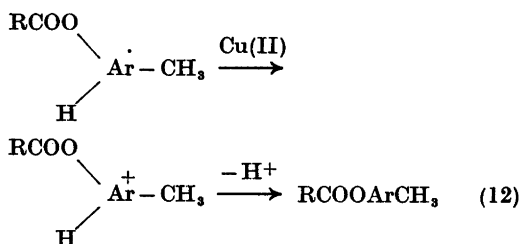
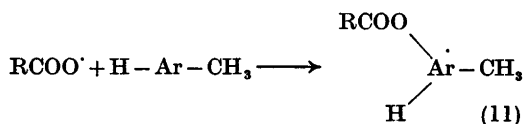
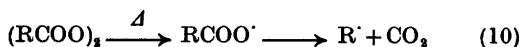
Table 8. Comparison between the product distribution from anodic acyloxylation and oxygenation by different peroxide/Cu(II) chloride systems of aromatic compounds.

Substrate	Anodic system	Isomer distribution, anodic acyloxylation			Isomer distribution, ( <i>i</i> -PrOCCO) <sub>2</sub> -CuCl <sub>2</sub> system			Isomer distribution (PhCOO) <sub>2</sub> -CuCl <sub>2</sub> system			Ref.	
		o	m	$\alpha$	o	m	$\alpha$	o	m	$\alpha$		
Toluene	AcOH/AcO <sup>-</sup>	43	11	46	57	15	28	6			22	
Toluene	MeCN/PhCOO <sup>-</sup>	24							56	18	26	66,67
Toluene	TfaoH/Tfao <sup>-</sup>	51	5	44	76							25
Isopropylbenzene	AcOH/AcO <sup>-</sup>	44	17	39	47	16	36	2				22,68
Isopropylbenzene	MeCN/PhCOO <sup>-</sup>	19		81	Trace							66
Mesitylene	AcOH/AcO <sup>-</sup>		80-96		19-4	93		7				69
Biphenyl	AcOH/AcO <sup>-</sup>	31	1	68	47	4	49					22,68
Naphthalene	AcOH/AcO <sup>-</sup>	96	4		92	8						22,68
Naphthalene	MeCN/PhCOO <sup>-</sup>	100										70
Anisole	AcOH/AcO <sup>-</sup>	67	4	29	63	<1	36		67	<1	33	22,67,71
Anisole	MeCN/PhCOO <sup>-</sup>	67		33					67	1	33	72,8
Fluorobenzene	AcOH/AcO <sup>-</sup>	34	8	58	33	22	45					22,68
Chlorobenzene	AcOH/AcO <sup>-</sup>	37	6	58	54	13	33					22,68
Benzotrifluoride	TfaoH/Tfao <sup>-</sup>	35	47	18	47	51	2					19a,68
Acetophenone	TfaoH/Tfao <sup>-</sup>	54	32	14	50	33	17					19a,68



7; proton abstraction by  $\text{AcO}^-$  is about  $10^4$  times faster than by water<sup>64</sup>). To complicate things further, oxidative acyloxylation *via* metal ions, except  $\text{Ag(II)}$  (see Tables 2–5), generally favors  $\alpha$  attack in spite of the fact that acetate ion is present in most of these reactions. As pointed out above, this behaviour might of course indicate that the mechanism here involves hydrogen atom abstraction by the metal ion and thus removes this particular problem from our immediate concern. But how are then the contradictory findings about the anodic acyloxylation reaction to be explained?

To illuminate this situation further, Table 8 compares cases of anodic acyloxylation with the corresponding cases of another type of process, oxygenation *via* diisopropyl peroxydicarbonate- or benzoyl peroxide-Cu(II) chloride in acetonitrile at 60 °C, the mechanism of which has been shown<sup>67,68</sup> to be represented by the reactions of eqns. 10–14 ( $\text{R} = \text{iPrO}$  or  $\text{Ph}$ ). Here an acyloxy radical of reasonable stability



(*e.g.*,  $E_a$  for decarboxylation of  $\text{PhCOO}^\cdot$  is <sup>13</sup> 60–75  $\text{kJ mol}^{-1}$ ) is formed (eqn. 10) and it then attacks the nucleus of the aromatic ring (eqn. 11) followed by electron transfer oxidation of the intermediate radical by  $\text{Cu(II)}$ . The side-chain substitution observed (Table 8) is considered to be due to hydrogen atom ab-

straction, not by  $\text{RCOO}^\cdot$ , but by  $\text{R}^\cdot$  formed *via* decarboxylation of  $\text{RCOO}^\cdot$ . (eqns. 13 and 14).<sup>73</sup>

Consideration anodic acyloxylation, let us for a start look at benzoyloxylation for which the composition of the rather complicated product mixture<sup>66,72</sup> strongly suggests that anodically generated benzoyloxy radical is the species responsible for the course of the reaction (eqn. 11). Comparison with the peroxide based reaction shows a great similarity between the two reaction types (a detailed comparison must await refinement of the experimental data). Proceeding to anodic acetoxylation, we again note a profound similarity with the peroxide based process, and it is then very tempting to assume that anodic acetoxylation occurs *via* anodically generated acetoxy radical as depicted in eqns. 10–14. Side-chain acetoxylation would then occur as a result of hydrogen atom abstraction by methyl radical (eqn. 13) and not *via* eqn. 1. A test of this part of the mechanism immediately suggests itself: With a suitably deuterated substrate,  $\text{ArCD}_3$ , the yield of  $\alpha$  acetoxylation product must be matched by the yield of  $\text{CH}_3\text{D}$  among the gaseous products. For acetoxylation without acetate ion present, the ordinary radical cation mechanism would be perfectly feasible.

We are well aware that the above reasoning does not represent the last word on the question of a direct *vs.* indirect mechanism for anodic acyloxylation and that most studies so far have pointed in the direction of a direct mechanism.<sup>1,3f</sup> An analysis<sup>13</sup> of the kinetics of decarboxylation of  $\text{R}-\text{COO}^\cdot$  and  $\text{R}-\text{OCO}^\cdot$  has, however, clearly shown that the choice between the two possibilities might hinge upon a very delicate balance between many kinetic parameters. In view of the contradiction unveiled above, we think that the balance now is slightly displaced toward the indirect mechanism. Hopefully, experiments designed from this perspective might give clues to a better understanding of this problem. In particular, the use of alkyl carbonate anions ( $\text{RO}-\text{COO}^-$ ) for anodic acyloxylation should provide illuminating insights into the mechanism, if the experimental problems can be solved.

Finally, we again<sup>3</sup> wish to draw attention to the analogy between the homolytic alkylation or arylation of aromatic compounds ( $\text{R}^\cdot + \text{Ar}$ ) and the reaction between the corresponding

carbanions and radical cations ( $R^- + Ar^+$ ). In view of the ease of oxidation of carbanions (in the form of organometallics, say  $RLi$  or  $RMgX$ ), one would predict that the reaction between a carbanion and a radical cation of even low oxidizing power would lead to very rapid initial electron transfer and hence that products would be derived from attack by  $R^-$  upon  $Ar$ . Somewhat surprisingly, such studies have to our knowledge not been performed before but should be of considerable interest, not least because of the present discussion regarding the polarity of radical substitution reactions which seems to determine the ratio between nuclear and  $\alpha$  attack,<sup>75,76</sup> a recurrent problem in oxidative substitution.

*Acknowledgements.* Financial support from the Swedish Natural Science Research Council is gratefully acknowledged. We thank Professor V. D. Parker, University of Trondheim, Norway for performing measurements of reversible potentials and Dr. J. Holeman, Risø National Laboratory, DK-4000 Roskilde, Denmark for communicating results prior to publication.

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Received May 9, 1978.