Kinetics of the Birch Reduction

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Because of contradictions in the literature, we reinvestigated the kinetics of the Birch reduction, i.e. the hydrogenation of benzene and its derivatives in metal ammonia solutions (MAS; containing solvated electrons e^- and metal cations M^+) with alcohols to yield the corresponding cyclohexa-1,4-dien compounds (e.g. $2 Li + 2 CH_3OH + C_6H_6 \Rightarrow 2 CH_3OLi + C_6H_8$). The kinetics of this reaction are obscured since the hydrogen reaction proceeds parallel to it ($2 Li + 2 CH_3OH \Rightarrow 2 CH_3OLi + H_2$). The two reactions differ in their activation energies (6.5 and 22.5 kJ/Mol resp.); and in the series of the alkali metals Li, Na and K the rate of the Birch reduction decreases, whereas that of the hydrogen reaction increases. However, in the metal concentration range around 0.01 M, both reactions have within the experimental error the same reaction order with respect to the metal (≈ 0.8). Both are accelerated by addition of alkali cations common to the dissolved alkali metal, and both are decelerated by addition of alkali cation complexing cryptands. Thus we conclude that the cations are involved in the kinetics of both reactions, probably by forming intermediate ion pairs or shifting pre-equilibria in which solvated electrons are involved. The experimental data of both reactions can be described very well with the rate laws $v(B) = k_B f^2 [e^-][Li^+][CH_3OH][C_6H_6]$ and $v(H) = k_H f^2 [e^-][Li^+][CH_3OH]$ resp. (f activity coefficients after Debye-Hückel) inserting the concentrations of e^- and Li^+ as calculated from the known thermodynamics of LiAS. The experimental rate constants k_B and k_H are the products of the rate constants of the rate determining steps and the equilibrium constants of the pre-equilibria.

1. Introduction

The Birch reduction [1] is a very powerful tool for the hydrogenation of benzene and its derivatives to yield the cyclohexa-1,4-dien compounds. It is performed in metal ammonia solutions (MAS, electron donor) with added alcohols (proton donor), e.g.:

$$2 Li + 2 CH_3OH + C_6H_6 \Rightarrow 2 LiOCH_3 + C_6H_8 \qquad (1)$$
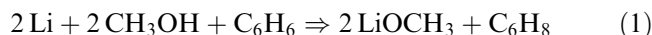
The Birch reduction is in contrast to the catalytic hydrogenation that leads to the corresponding fully hydrogenated compound, e.g.:

$$3 H_2 + C_6H_6 \Rightarrow C_6H_{12} . \qquad (2)$$

In spite of its importance for the organic chemist, only little and partly contradicting information about the kinetics of the Birch reduction is found in the literature. Krapcho and Bothner-By [2] give on the basis of their experiments the third order rate law

$$v = -d[B]/dt = d[BH_2]/dt = k[M][A][B] \qquad (3)$$

(B benzene or toluene, BH_2 its hydrogenated Birch-product, M dissolved alkali metal, A ethyl-, propyl- or butylalcohol; chemical symbols in squared brackets stand for concentrations; equivalent concentrations of the three reactants, $[M] \approx 0.2$ M). Jacobus and Eastham [3] put some doubts on this rate law because the hydrogen reaction, e.g.

$$2 Li + 2 CH_3OH \Rightarrow 2 LiOCH_3 + H_2 \qquad (4)$$

which always will proceed parallel to reaction (1) was neglected. From their experiments with lithium and ethylalcohol they derive the fourth order rate law

$$v = k[M]^2[A][B] . \qquad (5)$$

Further experimental results are: the yield of the Birch reduction increases in the series of the alkali metals K, Na, Li [2, 3], the Birch reduction is faster with ethanol than with butanol [2], it is accelerated by addition of alkali bromides with cations common to the alkali metal solution [2], and it has a very low activation energy [2].

At the time of publication of the two papers it was known already that MAS do not contain neutral atoms M° of the dissolved metal as major component but rather metal cations M^+ and paramagnetic solvated electrons e^-, formed by ionisation of the metal, and a diamagnetic species of not known stochiometry with two spin paired electrons [4]. With this knowledge rate law (5) was reinterpreted by Dewald [5] with the assumption that in an intermediate reaction step $B + e^-$ form a radical anion B^- which, with the cation, yields an ion pair ($M^+ B^-$). This then is protonated by the alcohol (see Eq. (15)–(19)). Justification for this reaction sequence follows from studies on the protonation of aromatic radical anions in solvent systems of lower dielectric constant [6]. Dewald gives the rate law

$$v = k[e^-][M^+][A][B] . \qquad (6)$$

It is identical with Eq. (5) in case of highly diluted MAS in which all metal is dissociated into M^+ and e^- ($[M^+] = [e^-] = [M]$). However the experiments [3] were performed at metal concentrations around 0.1 M, that is at least 100 times too high to allow the assumption of complete dissociation of the dissolved metal [7]. Thus Dewalds interpretation of rate law (5) is intuition only, but a good one as we will see later.

There is one contradiction in the literature concerning the action of the alcohol. The reaction rate in the rate laws (3), (5), and (6) is proportional to the alcohol concentration, which should be interpreted that the alcohol molecules A are part of the reaction scheme. On the other hand, it is stated that the reactions are decelerated by addition of alkali alcolates [3]. This is interpreted by Jolly [8] with the assumption that not the alcohol is the protoning particle, but NH_4^+ formed in the dissociation equilibrium $(ROH+NH_3 \Leftrightarrow RO^- + NH_4^+)$ which is shifted to the left by the addition of RO^- ions, thus decelerating the reaction.

At higher metal concentrations rate law (6) can be evaluated only if the concentrations of the cations and solvated electrons in MAS are known. In our earlier potentiometric studies on NaAS and LiAS [7] we succeeded in revealing the thermodynamics of these systems and in interpreting it on the basis of solvated electrons, cations and of the species $(e^- M^+ e^-)$ which is the complex of two spin paired electrons and a cation (in the following abbreviated by M^-). We attained no thermodynamic evidence for an ion pair $(M^+ e^-)$ which might be present as a minority component (symbolised as M°). From the thermodynamic data we can calculate the concentrations of the involved species for a wide metal concentration and temperature range.

With this understanding of the MAS, we thought it worthwhile to reinvestigate the Birch reduction together with the unavoidable hydrogen reaction, varying the nature and the concentration of the alkali metal (Li, Na, K) and of the alcohol (CH_3OH, C_2H_5OH, C_3H_7OH, (and H_2O)), and varying the concentration of C_6H_6, and finally varying the temperature, all in a wide range.

2. Experimental Part

The reaction flask of an inner volume of around 300 ml was made of glass. It was surrounded by a glass mantle through which the cooling liquid of a cryostat was circulated (for all experiments 217 ± 0.1 K, unless stated differently). On top it was equipped with several ground joints for connection to the vacuum line and to a differential gage (Baratron pressure meter 210, MKS-Instruments), and for housing a thermocouple and a septum. A glass valve was attached to the bottom of the flask.

Liquid ammonia and the alkali metals were purified and the MAS were prepared in the reaction flask as described before [7]. Benzene, dissolved in diethyl ether to enhance its solubility in ammonia, and alcohols, all of highest purity available, and water, after repeated distillation, were all degassed by pump freezing before adding them with the help of a syringe through the septum to the MAS which was agitated by a magnetic stirrer.

The hydrogen reaction was followed by continuous pressure registration with the differential gage, the reference cell of which was connected to the vacuum line. The pressure reading was done with an uncertainty of 2 Torr. Assuming that (with an excess of alcohol) all metal com-

pletely reacts under formation of hydrogen, its increasing pressure in the flask is directly related to the decreasing metal concentration: $[M(t)]=[M(0)] (1-p(t)/p(\infty))$ with $[M(i)]$ metal concentration at time t and $t=0$ and $p(i)$ hydrogen pressure at t and $t=\infty$.

The Birch reduction was followed discontinuously by taking liquid samples from the reacting solution through the bottom valve. After quenching the reaction by adding an excess of solid sodium benzoate to the sample [2], C_6H_6 and C_6H_8 were extracted with diethyl ether. For the analysis of C_6H_6 and C_6H_8, the etheric solution was injected through a septum into a gas chromatograph (Hewlett Packard HP5890 with flame ionisation detector) which was calibrated with proper solutions of the corresponding compounds. The uncertainty of the analysis was 5%.

3. Experimental Results

Hydrogen Reaction. The progress of reaction (4) with Li, Na, and K, with Li and added LiBr, all with methanol as proton donor follows from Fig 1. Due to an alcohol excess, the concentration of the alkali metals goes down to zero. In all further experiments in which we varied the concentration or the nature of the metal or the alcohol, in which we added electrolytes or changed the temperature, we got the same characteristic kinetic curves as in Fig. 1, i.e. a change from a low to a high relative reaction rate $(d(\ln c)/dt)$ after the metal concentration decreased below 10^{-4} M. Therefore we will not reproduce any more of the many experimental curves obtained in this study but only describe their results.

The slope of the lines in the double logarithmic plot of the initial rate v for the three metals and their concentrations in Fig. 2 ($v=$ const $[M]^m$ or $\log(v)=\log(\text{const})+m \log[M]$) reveals that the reaction order m with respect to the metals is definitely smaller than unity, namely
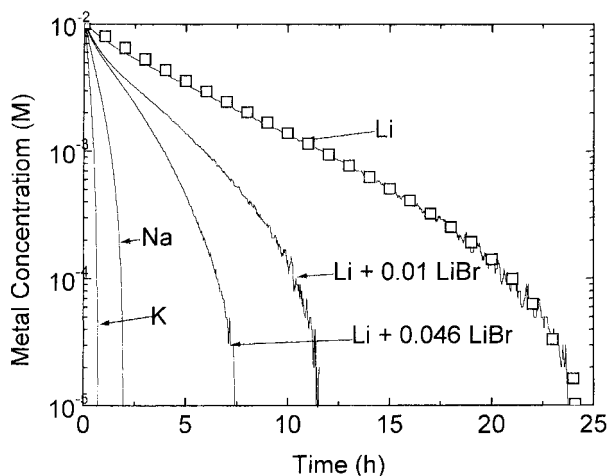

Fig. 1
Hydrogen reaction with lithium, sodium and potassium and lithium with added LiBr: time dependence of the alkali metal concentration (0.025 M CH_3OH). Full line: experimental curves, open squares: simulation of the reaction with rate law (14) for lithium
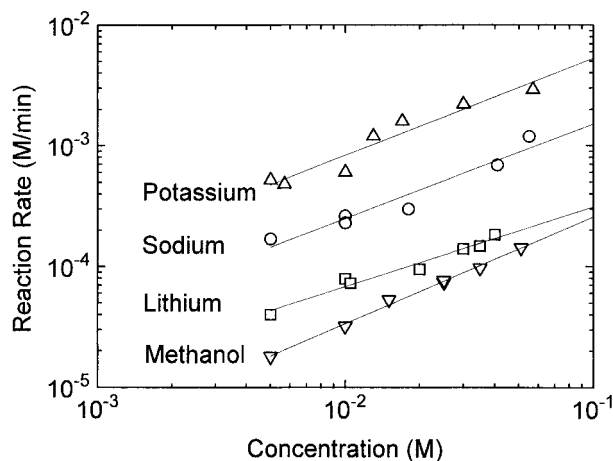
Fig. 2
Hydrogen reaction: double logarithmic plot of the initial reaction rate and the concentrations of lithium, sodium and potassium and of methanol resp. for the determination of their reaction order (0.025 M CH_3OH or 0.01 M alkali metal resp.)

Fig. 3
Hydrogen and Birch reaction: Arrhenius plot of the initial rates (0.01 M Li, 0.025 M CH_3OH, and 0.0035 M C_6H_6)

$m = 0.75 \pm 0.08$ as average. The reaction order with respect to methanol is taken from the same plot as 0.91 ± 0.03. We assume it to be 1 (although that is outside the limit of error) because a reaction order 0.9 for methanol does not make sense. Thus we formulate the rate law for the hydrogen reaction with Li ($=M$) and CH_3OH ($=A$)

$$-d\,[M]/dt = 2\,d\,[H_2]/dt = k_7\,[A]\,[M]^m\,(+k_z)$$
$$\text{(with } m = 0.75) \tag{7}$$

(the zero order rate constant k_z takes into account that catalytic acting impurities might accelerate the reaction as already described by Dewald [5]). From Fig. 2 we also read that at the metal concentration 0.01 M, the ratio of the relative rates of reaction (4) with Li, Na, and K is about 1:3.5:12. This reflects the known order of the reactivity of the alkali metals with respect to water or air, or also with respect to water [9] or alcohol [3] in ammonia or with respect to ammonia [10].

Similarly we also have a pronounced influence of the nature of the proton donator on the reaction rate: in the order methanol, ethanol and 2-propanol the relative rates with Li or Na are about 1:0.6:0.25 reflecting the decreasing proton donating power of the alcohols as expressed by their auto ionisation constants p_K (16, 18 and 19 resp. at 25 °C [11]). Of course the high stability of pure MAS fits in this pattern because of the very high p_K of ammonia (around 30) [12]. Water dissolved in ammonia however reacts considerably slower than expected on the basis of its $p_K = 14$; we have given an explanation for this previously [9].

Addition of Li salts (LiBr or $LiOCH_3$) to the reaction mixture with Li gives a pronounced increase of the reaction rate (a factor of 2 by adding 0.01 M LiBr to the 0.01 M Li + 0.025 M CH_3OH reaction mixture (Fig. 1)). The fast reaction with Na is strongly decelerated by 0.01 M LiBr addition, whereas the slow reaction with Li is
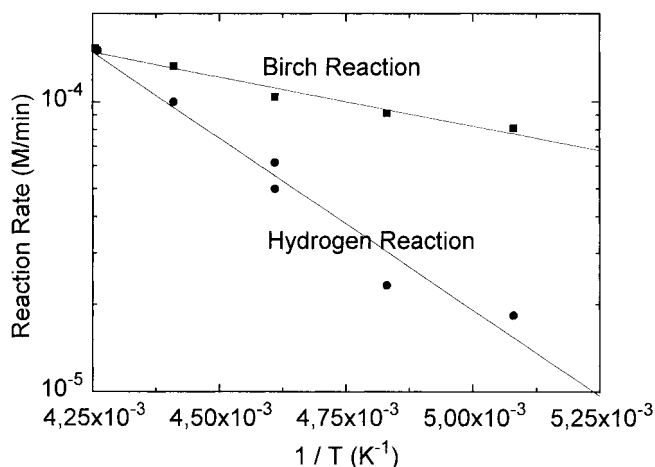
slightly accelerated by NaBr, such that within the experimental error in both cases (with identical metal and electrolyte concentrations) the same reaction rate is observed which is between that of a Li and a Na reaction system of the same metal concentration without electrolyte. Addition of alkali cation complexing cryptands e.g. 4,7,13,18-tetraoxa-1,10-diazabicyclo-[8.5.5]eicosan (trade name Kryptofix 211 or C211) to Li solutions, C221 to Na solutions or C222 to K solutions, all with methanol as proton source, results in a pronounced decrease of the reaction rate (a factor of 4 in case of 0.01 M Li with 0.02 M C211). All this definitely shows that the cations are involved in the kinetics, probably by forming ion pairs or complexes with the reacting particles. – From the Arrhenius plot in Fig. 3 we gain an experimental activation energy of 22.5 ± 2.2 kJ/mol for the hydrogen reaction.

Birch Reduction. The Birch reduction of benzene (leading to 1-4 cyclohexadien) can never be observed as such but only in competition to the hydrogen reaction. Due to this competition the yield of the Birch product depends on the relative rates of the two reactions. It is the larger, the faster the Birch reduction relative to the hydrogen reaction. – The yields of the other possible reduction products 1-3-cyclohexadien and cyclohexadien are below 1% and therefore can be neglected in the further considerations.

From Fig. 4 we read that the rate and the yield of the Birch reduction very strongly depend on the nature of the alkali metal. The Birch reduction is fastest with Li and slowest with K, the ratio of the initial rates with Li, Na and K is about 13:1.2:1 whereas the hydrogen reaction is fastest with K and slowest with Li (Fig. 1). Consequently the yield of the Birch product (referred to the initial concentration of benzene) is largest with Li ($\approx 71\%$), intermediate with Na ($\approx 11\%$) and smallest with K ($\approx 7\%$).

In all further experiments in which we varied the concentrations or the nature of the metal and of the alcohol,
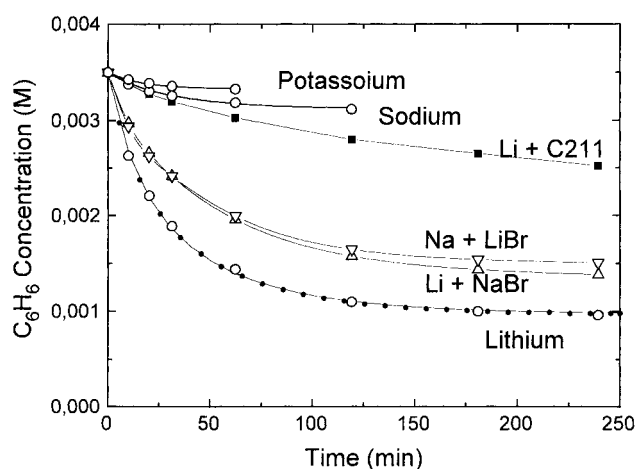
Fig. 4
Birch reduction: Time dependence of the benzene concentration with lithium, sodium, or potassium (0.01M), with Li+NaBr or Na+LiBr (0.01 M each), with Li (0.01 M)+cation complexing cryptand C221 (0.02 M); (methanol 0.025 M). Open symbols and ■: experimental points; full lines: simulation for Li, Na and K with rate laws (7) and (8) with $n = m = 0.8$; full circles: simulation for Li with rate laws (14) and (19)

Fig. 5
Birch reduction: double logarithmic plot of the initial reaction rate and the concentrations of lithium (fixed concentrations: 0.025 M CH_3OH, 0.0035 M C_6H_6), methanol (0.01 M Li, 0.0035 M C_6H_6), and benzene resp. (0.01 M Li, 0,025 M CH_3OH) for the determination of their reaction order

in which we added electrolytes or cation complexing cryptands, or changed the temperature, we got the same characteristic kinetic curves as in Fig. 4, i.e. a steady decrease of the reaction rate ($-d[B]/dt$) from its fastest initial value to zero when all metal is consumed. Therefore we will not reproduce any further experimental curves but only describe their results.

The double logarithmic plot of the initial rates of the Birch reduction and the concentrations of the reactants in Fig. 5 reveals that the reaction order with respect to methanol and to benzene is 0.99±0.05 and 1.05±0.05 resp., i.e. both are unity, and that of Li is about $n = 0.82 \pm 0.03$. Thus we formulate the formal rate law for the Birch reduction:

$$2\,d\,[BH_2]/dt = -2\,d\,[B]/dt = k_8\,[A]\,[B]\,[M]^n$$
$$(\text{with } n = 0.82).\tag{8}$$

The rate of the Birch reduction depends as strongly as that of the hydrogen reaction on the nature of the alcohol. In the order methanol, ethanol and 2-propanol the relative rates of the Birch reduction with Li or Na are about 1:0.55:0.15, close to that of reaction (4). Addition of Li salts (LiBr or $LiOCH_3$) to the reaction mixture with Li gives a moderate but definite increase of the reaction rate. As shown in Fig. 4 the slow reaction with Na is accelerated by LiBr, whereas the fast reaction with Li is delayed by NaBr, such that within the experimental error in both cases (with identical metal and electrolyte concentrations) the same reaction rate is observed which is between that of an Li and an Na reaction system of the same metal concentration without electrolyte. Addition of alkali cation complexing cryptands e.g. C211 to Li solutions (Fig. 4), C221 to Na solutions or C222 to K solutions, all
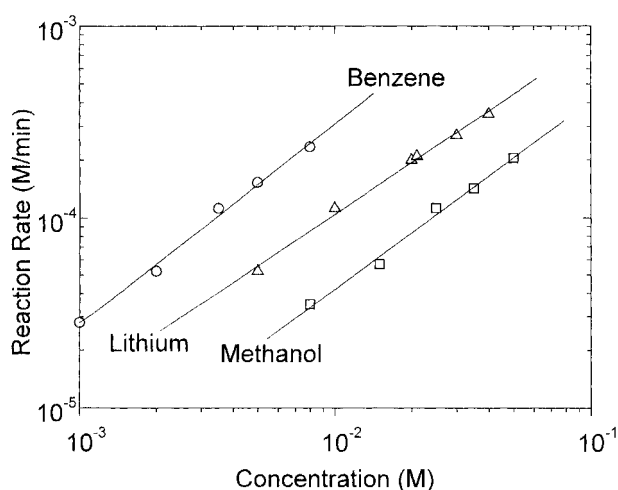
with methanol as proton source, results in a pronounced decrease of the reaction rate (a factor of 10 in the case of 0.01 M Li with 0.02 M C211). All this definitely shows that the cations are involved in the kinetics, probably by forming ion pairs or complexes with the reacting particles. – From the Arrhenius plot in Fig. 3 we obtain an experimental activation energy of 6.5±0,7 kJ/mol for the Birch reduction in fair agreement with 11.3 kJ/mol obtained by Krapcho and Bothner-By [2].

4. Evaluation of the experimental results

Formal Kinetics. Formally in both reactions the metal reduces alcohol to hydrogen which in the Birch reduction is transferred to benzene B forming BH_2 or which in the hydrogen reaction is liberated as H_2. Therefore we might expect that both reactions follow the same formal kinetics, i.e. that their rate laws (7) and (8) should have not only the same reaction order with respect to the alcohol (we found 0.91±0.03 and 0.99±0.05 and set both 1.00) but also with respect to the metal, or $m = n$, as almost is experimentally found with $m = 0.75 \pm 0.08$ and $n = 0.82 \pm 0.03$.

Indeed the iterative integration of the coupled differential equations (7) and (8) with suitably chosen rate constants k_7 and k_8 gives a very good fit of the experimental data of the Birch reduction in Fig. 4 with $m = n = 0.8$ (about the average of the experimental data given in the last section) as shown by the smooth curves in Fig. 4 (for Li, Na, and K resp.: $k_8 = 52$, 6 and 5 $M^{-1.8}/min$, $k_7 = 0.1$, 0.25 and 0.5 $M^{-0.8}/min$). The fit becomes less satisfactory or even fails with m or n or both deviating more than 0.05 from the given average.
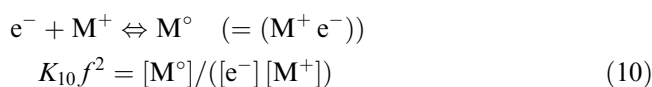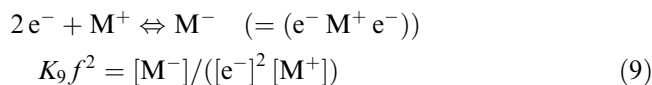
With the reaction order $m = 0.8$ for the hydrogen reaction (Fig. 1) we can fit the experimental data only down

to a metal concentration of about 10^{-4} M; below this the reaction is slightly faster than calculated, probably due to the additional zero order reaction as already described by Dewald [5] and explained by unavoidable catalytic acting impurities. A good fit of the experimental data is obtained for Li with $k_7 = 0.05$ M$^{-0.8}$/min and the additional zero order rate constant $k_z = 1 \cdot 10^{-7}$M/min. With corresponding larger rate constants we can simulate the kinetic curves for Na and K.

The results of the simulations justify our assumption that both reactions (1) and (4) for all three metals very closely have the same reaction order with respect to the metal (however rate constant k_7 obtained from the treatment of the Birch reduction disagrees with that directly obtained for the hydrogen reaction by a factor of about 2. We think this is not due to experimental errors, but to the fact that in both reactions we deal with slightly different systems: for the Birch reduction we added diethyl ether to enhance the solubility of benzene).

Detailed Kinetics. Although we think that we can simulate the experimental data for the hydrogen reaction and the Birch reduction with the formal rate laws, we still have no information on their real kinetics. The only information we attained is that both reactions have, within the experimental error, the same reaction order with respect to the metal; thus we can conclude that in both reactions the same reactive species are involved.

We recall that alkali metals dissolved in ammonia form solvated electrons e$^-$ and cations M$^+$, the complex of two spin paired electrons with a cation, symbolised as M$^-$ and perhaps, as a minority component, the neutral complex of an electron and a cation, symbolised as M$^\circ$. Thus we can formulate the equilibria (f ion activity coefficients calculated according to the Debye-Hückel theory)

$$2\,e^- + M^+ \Leftrightarrow M^- \quad (= (e^-\,M^+\,e^-))$$
$$K_9 f^2 = [M^-]/([e^-]^2\,[M^+]) \tag{9}$$

$$e^- + M^+ \Leftrightarrow M^\circ \quad (= (M^+\,e^-))$$
$$K_{10} f^2 = [M^\circ]/([e^-]\,[M^+]) \tag{10}$$

$$M^+ + M^- \Leftrightarrow 2\,M^\circ \tag{11}$$

In the metal concentration range we are working in, equilibrium (9) is shifted to the right with increasing metal concentration [7], i.e. the concentration of M$^-$ increases stronger than the metal concentration; if M$^-$ were the reactive particle in the reactions we should have a reaction order larger than 1 with respect to the metal. Since it is around 0.8 we can exclude M$^-$ as the reacting species; we already have done this for the hydrogen reaction with water in an earlier study [9]. Furthermore we recall that addition of electrolytes with the same cations as the reacting metals increases and that addition cation complexing cryptands decreases the rates of both reactions. This implies that the cations are directly involved in the kinetics.

Thus we conclude that e$^-$ together with M$^+$ or M$^\circ$ resp. formed in equilibrium (10) as a minority component are part of the schemes of both reactions and we set the following reaction sequences.

Hydrogen Reaction. M$^\circ$ from equilibrium (10) reacts with alcohol in the rate-determining step to yield H atoms which very fast recombine to H$_2$

$$M^\circ + ROH \Rightarrow H + RO^- + M^+ \text{ (rate determining)} \tag{12}$$
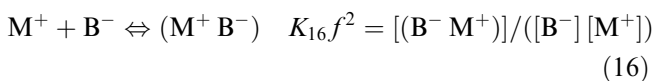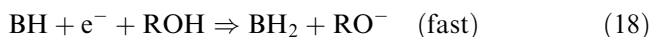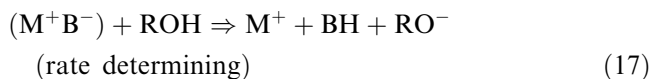
$$2\,H \Rightarrow H_2 \qquad \text{(fast)} \tag{13}$$

M$^\circ$ as intermediate reacting species has been postulated before on the basis of kinetic studies by pulse radiolysis in metal ammonia solutions [13] and in aqueous systems [14]. The rate law then is (k_i, K_i rate and equilibrium constants of reaction i)

$$
\begin{aligned}
-d\,[M]/dt = 2\,d\,[H_2]/dt &= k_{12}\,[M^\circ]\,[A]\,(+k_z] \\
&= k_{12}\,K_{10}f^2\,[e^-]\,[M^+]\,[A]\,(+k_z) \\
&= k_H f^2\,[e^-]\,[M^+]\,[A]\,(+k_z). \tag{14}
\end{aligned}
$$

We combine the individual rate and equilibrium constants in the experimental rate constant $k_H = k_{12}K_{10}$. Since we know the equilibrium constant $K_9 = 4.9 \cdot 10^4$ M^{-2} at 217 K [7] we can under consideration of the activity coefficients calculate the concentrations of e$^-$ and M$^+$ in LiAS in the concentration range covered in our experiments. Thus we can evaluate rate law (14) by iterative integration (at reaction start with a 0.01 M LiAS we have [e$^-$] = 5.1 $\cdot 10^{-3}$ M, [Li$^+$] = 7.6 $\cdot 10^{-3}$ M and [Li$^-$] = 2.4 $\cdot 10^{-3}$M with $f = 0.5$). We can fit the experimental data only by taking into account that Li$^+$ ions form with CH$_3$O$^-$ ions undissociated ion pairs or molecules (CH$_3$O$^-$ + Li$^+$ $\Leftrightarrow$ CH$_3$OLi, association constant K_a) with $K_a = 1500$ M^{-1} (this is comparable to the association constants of any normal electrolyte in ammonia as determined by conduction experiments [15]). The result of the simulation for lithium with $k_H = 150$ M^{-2} min^{-1} and $k_z = 3 \cdot 10^{-7}$ M/min is given in Fig. 1 (open squares); it fits the experimental data excellently.

Birch Reduction. Higher aromatic compounds yield in metal ammonia solutions radical anions in high concentrations [16, 17]. With benzene B however the corresponding equilibrium (15) is far on the left [18], such that the benzene radical anion B$^-$ cannot be detected with any analytical means. We revive the suggestion from Dewald [5] that B$^-$ forms an ion pair with the cation, whereby equilibria (15) and (16) are shifted to the right. Protonation of the ion pair is rate determining; the final formation of cyclohexa-1,4-dien proceeds very fast:

$$B + e^- \Leftrightarrow B^- \quad K_{15} = [B^-]/[B]\,[e^-] \tag{15}$$

$$M^+ + B^- \Leftrightarrow (M^+\,B^-) \quad K_{16} f^2 = [(B^-\,M^+)]/([B^-]\,[M^+]) \tag{16}$$

$$(M^+ B^-) + ROH \Rightarrow M^+ + BH + RO^-$$

$$\text{(rate determining)} \quad (17)$$

$$BH + e^- + ROH \Rightarrow BH_2 + RO^- \quad \text{(fast)} \quad (18)$$

Thus we obtain the rate law

$$2\,d\,[BH_2]/dt = -2\,d\,[B]/dt = k_{17}\,[M^+ B^-]\,[A]$$
$$= k_{17}\,K_{15}\,K_{16}\,f^2\,[e^-]\,[M^+]\,[A]\,[B]$$
$$= k_B\,f^2\,[e^-]\,[M^+]\,[A]\,[B]\,. \quad (19)$$

We combine the individual rate and equilibrium constants in the experimental rate constant $k_B = k_{17}\,K_{15}\,K_{16}$. In order to avoid guesswork on the rate constants k_H and k_B we estimate their ratio from experimental data: dividing Eq. (14) by Eq. (19) and rearranging we get

$$d\,[H_2] = -k_B/k_H\,d\,[B]/[B] \quad (20)$$

(neglect of the zero order rate constant of Eq. (14) does not affect the further results). Integration within the boundaries $[H_2] = 0$ and $[B] = [B]^\circ$ at $t = 0$ and $[H_2]^\infty = 1/2\,[M]^\circ - [BH_2]^\infty = 1/2\,[M]^\circ - [B]^\circ + [B]^\infty$ and $[B] = [B]^\infty$ at $t = \infty$ yields

$$k_H/k_B = \ln\left([B]^\circ/[B]^\infty\right)/(1/2[M]^\circ - [B]^\circ + [B]^\infty) \quad (21)$$

We use the data of Fig. 4 for Li: $[M]^\circ = 0.01$ M, $[B]^\circ = 0.0035$ M, $[B]^\infty = 0.00094$ M and get $k_B/k_H = 540$ M^{-1}. From the initial rate of the Birch reduction 1, 1 10^{-4} M/min (Fig. 5) and the initial concentrations of the reaction partners and the activity coefficient all given above, we get $k_B = 1.3\ 10^5$ M^{-3} min^{-1} and thus $k_H = 240$ M^{-2} min^{-1} (in the evaluation of the hydrogen reaction in Fig. 1 we got $k_H = 150$ M^{-2} min^{-1}, see above). We now can evaluate the coupled rate laws (14) and (19) by iterative integration to obtain the time dependence of the benzene concentration in the Birch reduction. The result is displayed in Fig. 4 (filled circles). Again we have a very good fit of the experimental data for lithium. We did not try to fit the data for potassium and sodium, because these have a low yield of the Birch reduction and therefore are of minor interest only.

There remains one contradiction to the literature: according to Jolly [8] and Dewald [5, 19] the Birch and the hydrogen reaction proceed via NH_4^+ ions formed by dissociation of the alcohol or water ($ROH + NH_3 \Leftrightarrow NH_4^+ + RO^-$). Their concentration is at reaction start proportional to the square root of the alcohol concentration (Ostwald's dilution law). Consequently the initial reaction rate should be proportional to square root of the alcohol concentration (reaction order 1/2 with respect to alcohol) whereas we found a linear relation between the initial reaction rate and alcohol concentration (reaction order 1, see Fig. 2 and 5). Furthermore we could not observe the delay of the two reactions by adding RO^- ions (e.g. $LiOCH_3$) as has been reported by others [3] and has been explained by the

shift of the above dissociation equilibrium to the left resulting in a decrease of NH_4^+ ion concentration. Furthermore the equilibrium constant for $H_2O + NH_3 \Leftrightarrow NH_4^+ + OH^-$ in ammonia is $< 1 \cdot 10^{-20}$ [20] and thus the NH_4^+ concentration is too low to allow the hydrogen reaction with water to proceed via NH_4^+ ions. Indeed in our kinetic studies [14] we could exclude NH_4^+ ions as reaction partner at least for the hydrogen reaction with water. Since the dissociation constant of alcohols in ammonia hardly will be larger than that of water, we think that also the reaction with alcohols should not proceed via NH_4^+ ions. Finally we did not succeed in simulating any of the kinetic curves with rate laws including NH_4^+ ions. Thus we conclude in contrast to the arguments by Jolly and Dewald that not NH_4^+ ions but the undissociated alcohols are the reactive protoning partners in reaction (1) and (4).

5. Conclusions

As we have shown we can fit the experimental data of both reactions: for the hydrogen reaction we assume the pre-equilibrium (10) forming the ion pair ($M^\circ = (M^+ e^-)$) which in the rate determining step (12) reacts with ROH; and for the Birch reduction we assume the pre-equilibria (15) and (16) forming the ion pair ($M^+ B^-$) which in the rate determining step (17) reacts with ROH. However we do not think that the successful simulation proves beyond any doubt the given reaction mechanism, since we have to fit several constants, e.g. for the hydrogen reaction the zero order rate constant k_z, the rate constant k_H and the association constant K_a (the equilibrium constant K_9 vital for calculating the concentration of M^+ and e^- in MAS has been obtained from potentiometric measurements and should be correct). Also, we use activity coefficients calculated according to the Debye-Hückel theory that, in the concentration range of our experiments, might not be applicable anymore. Another reasonable reaction mechanism with several constants to choose also might give a satisfactory simulation.

We rather think the reaction mechanism – already proposed intuitively by Dewald [5] – is proven by our and other's [2] observation that the rate of the reactions is increased by addition of electrolyte having the same cation as the applied MAS, and by our observation that the addition of cation complexing agents decreases the reactions rates.

The different equilibria involved in the two reaction schemes (e.g. tight ion pairs M° and loose ion pairs ($M^+ B^-$) resp.) and/or the differences in the rate determining reaction steps might explain

a) that the rate of the Birch reduction increases, that of the hydrogen reaction decreases with the metals in the order K, Na, Li,

b) that both have different activation energies,

c) that Na^+ ions decelerate the fast Li-Birch reduction and Li^+ ions accelerate the slow Na-Birch reduction, and

d) conversely that Na$^+$ ions accelerate the slow Li-hydrogen reaction and Li$^+$ ions decelerate the fast Na-hydrogen reaction.

As physical chemists we can make the following recommendations to the organic chemist with respect to the Birch reduction:

a) use lithium as reductive agent, because with it the ratio of the rates of the Birch reduction and the hydrogen reaction and consequently the yield of the Birch product is larger than with the other alkali metals (Fig. 4);
b) apply the lowest possible temperature (most conveniently dry ice), because the ratio of the rates of the Birch reduction and the hydrogen reaction and consequently the yield of the Birch product increases with decreasing temperature (Fig. 3);
c) use methanol as protoning agent, which ensures the fastest reaction and for which the ratio of rates of the two parallel reactions and consequently the yield of the Birch product is about the same as with higher alcohols.

As we read in the extensive literature [21] most organic chemists have for a long time already carried out the Birch reduction under the conditions we recommend, but actually they do not know the reasons why they do so.

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