Kinetics and Mechanism of the Sodium–Ammonia Reduction of 2,2,4,4-Tetramethylpentan-3-one

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The kinetics of the reaction of sodium with 2,2,4,4-tetramethylpentan-3-one (TMP) in liquid ammonia was studied using the stopped-flow technique. The reactions were found to obey the fourth-order rate law $-d[e^-_{am}]/dt = 2k[e^-_{am}]^2[\text{ketone}][Na^+]$. The reaction rate was markedly reduced by addition of 2,2,2-cryptand. The addition of a weak acid (ethanol) had no effect on the observed rate. A mechanism involving ion-pairing with dianion formation being the rate-determining step is suggested. When TMP was initially exposed to an excess of lithium amide in liquid ammonia, the resulting mixture was found not to react with the ammoniated electron.

The mechanism and stereochemistry of active metal reductions of ketones, particularly cycloalkanones, has been the focus of considerable attention in recent years. Excellent review articles are available.[1–3] One longstanding controversy resulted from the original suggestion of Barton[4] that these reductions occur *via* dianions formed by a stepwise two-electron reduction of the ketone. House,[3] on the other hand, pointed out that the reduction potentials of the alkali-metals are probably not sufficient to form vicinal dianions from saturated aliphatic ketones. Therefore, House proposed that the reduction proceeds through a radical anion which is protonated by an added proton source (usually an alcohol). This protonation reduces electron–electron repulsion associated with dianion formation when a second electron is added to a radical anion. The House mechanism can be summarized by equations (1)—(4). Moreover, House[3] pointed out that the negative charge on

$$R_2CO + e^-_{am} \longrightarrow R_2CO^{-}\cdot \qquad (1)$$

$$R_2CO^{-}\cdot + R'OH \longrightarrow R_2COH\cdot + R'O^- \qquad (2)$$

$$R_2COH\cdot + e^-_{am} \longrightarrow R_2COH^- \qquad (3)$$

$$R_2COH^- + R'OH \longrightarrow R_2CHOH + R'O^- \qquad (4)$$

the radical anion could also be neutralized by tight association with a metal cation.

In a recent review, Pradhan[1] has pointed out that only a dianion mechanism can explain the available data for the reduction of saturated ketones by metals in ammonia in the absence of added proton donors. Huffman[5,6] has subsequently refuted the conclusions of Pradhan. Huffman[2] had earlier proposed that the House mechanism was operative with a modification which involves ion-pairing of the ketyl radical by the metal cation. Based on product studies and the conclusions of Hirota,[7] Huffman proposed that ketyl radical ion-pairs form dimers and higher aggregates, and that the spatial orientation of these ion aggregates leads to the observed stereochemistry of the products. According to Huffman,[2,5] the most compelling argument against the dianion mechanism is the insufficient reduction potentials of alkali-metals as suggested by House. Huffman[5] has also concluded that aliphatic ketones react with one equivalent of metal in an effectively irreversible reaction to form ketyls which are converted into the observed products without the intervention of dianions.

It is clear that a kinetic study would yield useful data necessary in resolving the present controversy. A rate expression that is first order with respect to the ammoniated electron (obtained by following the disappearance of e^-_{am}) would be consistent with Huffman's conclusions, while a rate expression that is second order with respect to the ammoniated electron would suggest a dianion mechanism.

To our knowledge, the only previous kinetic study of the metal–ammonia reduction of carbonyl derivatives was by Young and Dewald.[8] From a study of the sodium–ammonia reduction of *NN*-dimethylformamide (DMF) and *NN*-dimethylacetamide (DMA), Young and Dewald concluded that carbonyls are reduced *via* a dianion mechanism. They found that the reaction obeyed a fourth-order rate law (5). The step

$$\text{rate} = k[e^-_{am}]^2[\text{amide}][Na^+] \qquad (5)$$

involving dianion formation was suggested to be rate determining.[8] We undertook the present study to obtain more kinetic information concerning the metal–ammonia reduction of the carbonyl group. We have studied kinetically the sodium–ammonia reduction of a non-enolizable ketone, 2,2,4,4-tetramethylpentan-3-one (TMP).

Experimental

All work was done using high-vacuum techniques ($<10^{-5}$ Torr) in borosilicate glass systems. The titration experiments were performed at −34 °C in a thermostatted silicone fluid bath (Harris Mfg. Co.). Conductivity measurements were made using a Wayne Kerr B905 automatic precision bridge.

Materials.—Ammonia (Matheson) was purified by a method described previously.[9] Sodium (United Mineral) was purified by high-vacuum distillation.[8] Purified sodium samples of known weight sealed in glass breakseal tubes were prepared by a method described elsewhere.[10] TMP (Pfaltz and Bauer) was distilled repeatedly under vacuum onto a sodium mirror until a stable red solution persisted. TMP was then distilled under high vacuum into breakseal tubes and sealed off. The contents of these breakseal tubes were distilled into tared fragile glass ampoules or breakseal tubes and stored until use.[11] Purified ethanol and water samples were prepared by a procedure described elsewhere.[12]

2,2,2-Cryptand (PCR, Inc.), NaCl (Fisher), and NH_4Br (Aldrich) were used as received. Weighed samples of these reagents were prepared by placing the compound into a tared breakseal tube or fragile glass ampoule, evacuating, and sealing off under vacuum. Lithium amide was prepared from 2.5M-n-butyl-lithium in hexane (Aldrich) as received. Samples of an

Table 1. Summary of conductometric titration of 2,2,4,4-tetramethylpentan-3-one with sodium in liquid ammonia at −34 °C

Amount reacted at end-point		
10^4 Na (mol)	10^4 ketone (mol)	mol Na : mol ketone
1.63	1.70	0.96^a
1.20	1.30	0.92^a
1.42	1.32	1.1^b
0.963	0.977	0.99^b
55.7	51.1	$1.1^{b,c}$
2.50	1.26	$2.0^{b,d}$

[a] Ketone–NH_3 solution added to Na–NH_3 solution. [b] Na–NH_3 solution added to ketone–NH_3 solution. [c] Product analysis performed, see Table 2. [d] 0.363 mmol ethanol added to ketone–NH_3 solution prior to titration.

approximate number of moles were prepared by syringing a known volume of the liquid through a rubber septum and into a breakseal tube under argon. The breakseal tube was then placed in a dry ice–acetone bath and sealed off. Methylene dichloride (Baker) was used as received.

Apparatus.—Concentration *versus* time data were collected using an all-glass, low-temperature, high-vacuum stopped-flow apparatus.[13] The experimental operation of this apparatus has been described elsewhere.[14] The progress of the reaction was followed by monitoring the decay of the absorption of e^-_{am} with time at 1 000 nm. Beer's law has been reported to be valid for e^-_{am} and the molar extinction coefficient is 1.0×10^4 l mol^{-1} cm^{-1} at 1 000 nm.[15] Half the stopped-flow experiments were performed under pseudo-second-order conditions with respect to e^-_{am}.

Conductimetric titrations were performed by use of an apparatus and procedure described by Dewald and Jones.[16] Sodium concentrations were determined either from published conductivity data[9] or by using a weighed sodium sample. Titrations were performed both by adding the ketone–ammonia solution to the sodium–ammonia solution and *vice versa* (Table 1). Electrodes were sealed in both make-up vessels of the titration apparatus so that the conductivity of the metal solution could be measured regardless of whether the sodium–ammonia solution was added to the ketone–ammonia solution, or *vice versa*. Volumes of ammonia used were determined by first distilling ammonia into a calibrated vessel, and then distilling into the titration apparatus. It was assumed that there were negligible volume changes upon dissolution of the reactants. The course of the titration was followed by monitoring the conductivity of the solution. A titration was also performed by adding the sodium–ammonia solution to the ketone solution containing an added proton source (ethanol in excess of the ketone). In two experiments, TMP was initially exposed to lithium amide prior to titration with the Na–NH_3 solution. When n-butyl-lithium (in approximately ten-fold excess with respect to the ketone) was mixed with liquid ammonia (**CAUTION**! violent reaction) a suspension of lithium amide resulted. TMP was thoroughly mixed with the lithium amide–ammonia mixture, and the sodium–ammonia solution was added in the manner of a titration.

The reaction between TMP and sodium in the presence of the metal cation-complexing agent, 2,2,2-cryptand, was performed using an apparatus and procedures described elsewhere.[8] The sodium metal and the 2,2,2-cryptand were mixed together in ammonia in the metal make-up bulb, while the ketone was mixed with liquid ammonia in the substrate make-up bulb. The two bulbs were separated by a breakseal tube, which was broken to allow the two solutions to mix and initiate the reaction. The progress of the reaction was monitored by using a conventional conductimetric method[11] since the resulting slow reaction had a half-life >30 min. The determination of the absorption maximum for a reaction intermediate was done using an EG&G PAR model 1451 plasma monitor with a model 1452 1024-element diode array.

Analysis of Products.—Products were analysed using a Hewlett-Package Model 5992 gas chromatograph–mass spectrometer. Retention times and mass spectra were compared to authentic samples of TMP and 2,2,4,4-tetramethylpentan-3-ol. In experiments where the products were analysed (Table 2), TMP–ammonia solutions were titrated by adding the sodium–ammonia solution to the ketone or ketone–water solution. In the experiment in which no water was added to the ketone solution initially (Table 2) the ketone solution turned from clear to dark blue when the mol Na : mol TMP >1. At this time, the vessel was opened to atmosphere and the excess of e^-_{am} was quenched with ammonium bromide. Methylene dichloride was then added to the solution and the ammonia was allowed to evaporate. Finally, a portion of the remaining solution was analysed by g.c.–m.s. In the experiment where water was added to the ketone solution prior to titration, the ketone-containing solution turned dark blue for mol Na : mol ketone >2. This blue colour was bleached slowly (2—3 min), presumably due to the reaction between e^-_{am} and the proton source. The work-up in this experiment was identical to that described above.

Results

Table 1 gives a summary of the conductimetric titration experiments. In the absence of an added proton donor (ethanol or water), 1 mol of sodium reacted with 1 mol of TMP. After work-up, g.c.–m.s. analysis of the products showed 48% of the original ketone and 52% alcohol (Table 2). In a separate experiment, a positive test for ammonia by Nessler's reagent was observed upon acidification of the evacuated reaction products. In the presence of ethanol, 2 mol of sodium reacted with 1 mol of TMP (Table 1). G.c.–m.s. analysis shows that the products were 97% alcohol and 3% ketone (Table 2). Also, no apparent difference in the stoicheiometry was observed whether the sodium–ammonia solution was added to the ketone–ammonia solution, or *vice versa*.

When the liquid ammonia was first treated with n-butyl-lithium and then mixed with TMP, titration of the above mixture with a sodium–ammonia solution results in no observable reaction between the ketone and the ammoniated electron. Moreover, the observed increase in specific conductance of the mixture upon addition of the sodium solution agreed with the value calculated assuming that no reaction occurred.

After addition of a sodium–ammonia solution to a solution containing an excess of TMP, regardless of whether or not a proton source was present, a red-black transient solution which was bleached after a few seconds was observed. This transitory coloured solution was also observed in the stopping syringe during the stopped-flow experiments. This reaction intermediate was found to have an absorption band maximum at *ca.* 415 nm.

Figure 1 gives a typical pseudo-second-order plot, second order with respect to the ammoniated electron in the absence of a proton source. Also included in Figure 1 is a pseudo-first-order analysis, with respect to the ammoniated electron. In all experiments, linear plots were only obtained when the rate data were evaluated in terms of second-order kinetics with respect to the ammoniated electron. Figure 2 gives a typical pseudo-second-order plot with respect to the ammoniated electron in the presence of added ethanol as the proton source. Thus, a second-order dependence on the rate with respect to the ammoniated electron concentration is established both in the presence and absence of an added proton source. Table 3 gives a

Table 2. Results of product analysis for the reaction of sodium with 2,2,4,4-tetramethylpentan-3-one in liquid ammonia at −34 °C

Initial mmol of TMP	Initial mmol Na	Initial[a] mmol of H_2O added	% TMP[b] recovered	% 2,2,4,4-tetramethylpentan-3-ol recovered
5.11	5.57	none	48	52
3.32	excess[c]	4.89	3	97

[a] Initially added to ketone–NH_3 solution. [b] Determined by ratio of g.c. peaks (identified by m.s.). [c] The TMP–H_2O solution was titrated with Na–NH_3 solution until an excess of Na was added as evident by a persistent blue colour.

Table 3. Summary of the kinetic data for the reduction of 2,2,4,4-tetramethylpentan-3-one by sodium in liquid ammonia at −34 °C

10^3[ketone]/ mol dm^{-3}	$10^3[Na^+]^a$/ mol dm^{-3}	k_{obs}/dm^6 mol^{-2} s^{-1}	$\frac{k_{obs}/[Na^+]}{dm^9\ mol^{-3}\ s^{-1}}$
10.2	1.10	1.5×10^6	14×10^8
14.4	0.81	5.8×10^5	15×10^8
4.12	2.10	1.6×10^6	8×10^8
3.98[b]	2.23	2.1×10^6	10×10^8
10.8[c]	3.46	2.4×10^6	7×10^8
1.29	8.31[d]	9.6×10^6	12×10^8
3.41	0.90[e]	$<10^{-3}$	Av. $(11 \pm 3) \times 10^8$

[a] Calculated from conductivity of Na–NH_3 solution. [b] Ethanol (3.04×10^{-3}M) added to ketone solution. [c] Ethanol (5.70×10^{-3}M) added to ketone solution. [d] NaCl (5.61×10^{-3}M) added to ketone solution. [e] 2,2,2-Cryptand (8.21×10^{-3}M) added to sodium solution.

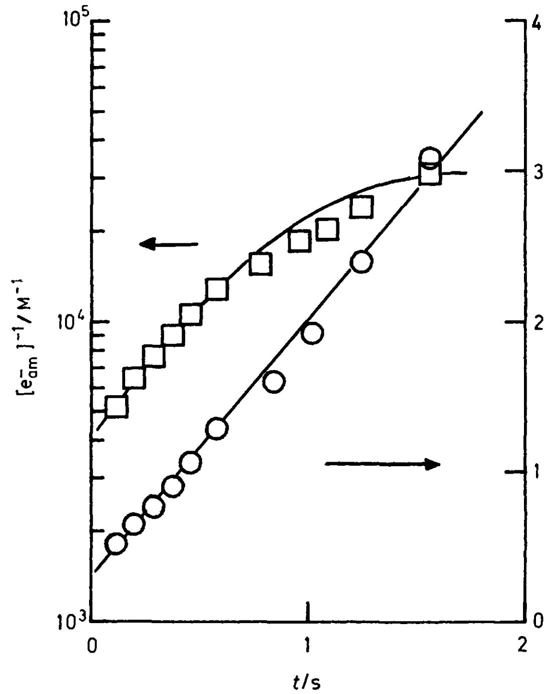

Figure 1. Plots of kinetic data for the reaction of TMP with e^-_{am}. Circles denote a pseudo-second-order analysis with respect to e^-_{am}. Squares represent a pseudo-first-order analysis with respect to e^-_{am}

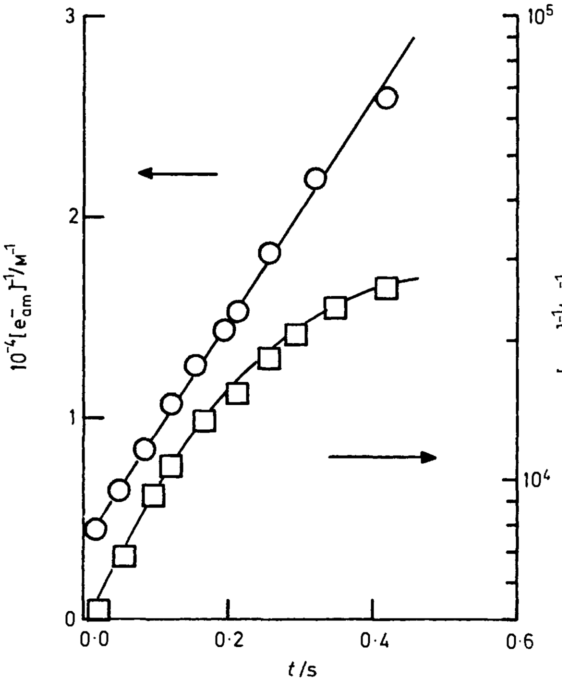

Figure 2. Plots of kinetic data for the reaction of TMP with e^-_{am} and added ethanol (5.70×10^{-3}M). Circles denote a pseudo-second-order analysis with respect to e^-_{am}. Squares denote a pseudo-first-order analysis with respect to e^-_{am}

summary of the kinetic data for the reactions of e^-_{am} with TMP.

While pseudo-second-order plots and the third-order plots gave an excellent representation of the experimental data, the third-order constants in Table 3 were found to vary directly with the sodium ion concentration. Log–log plots of k_{obs} *versus* the sodium ion concentration are shown in Figure 3. The sodium concentration (Table 3 and Figure 3) represents the total sodium ion concentration, *i.e.*, both the ion-paired and unpaired sodium cation concentration. Using the method of least squares, the slope of the straight line shown in Figure 3 was calculated to be 1.05 and hence a first-order dependence with respect to the sodium ion concentration is established.

Initial addition of the metal cation-complexing agent, 2,2,2-cryptand, to the sodium–ammonia solution drastically reduced the reaction rate (see Table 3).

Discussion

The consistency of the fourth-order rate constants (Table 3), the linearity of the pseudo-second-order plots (Figures 1 and 2), and the first-order dependence on the sodium ion concentration

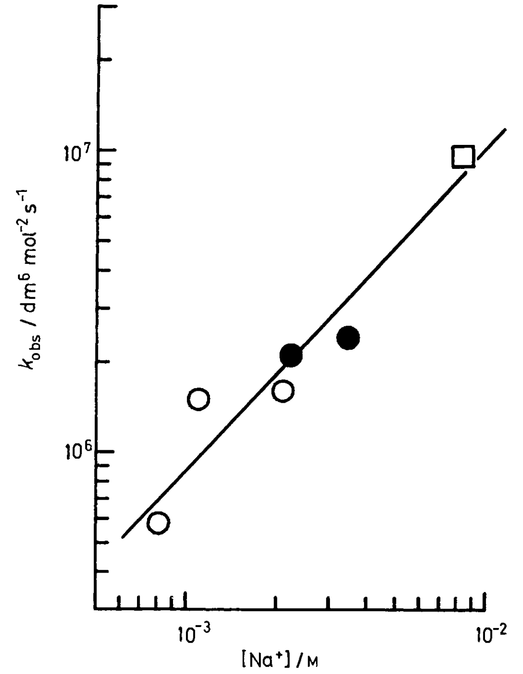

Figure 3. Log–log plots of the third-order rate constant *versus* [Na$^+$] for the reaction of TMP with e^-_{am}. Closed circles denote the experiments with added ethanol. Square denotes the experiment with added NaCl

(Figure 3) establish, for the concentration range investigated, that the rate law (6) holds. It was also observed that the addition of a proton source, ethanol, had no effect on the reaction rate (see Table 3). Therefore, we conclude that the protonation step, both in the presence and absence of an added proton donor, must follow the rate-determining step. The fact that the rate is independent of added proton source is in direct conflict with the mechanism proposed by House[3] where protonation of the ketyl is a key step. Also, Huffman's[2,5] modified dimer or higher aggregate mechanism, both in the presence or absence of a proton donor, cannot account for the experimentally determined rate expression or the observation that the rate is independent of added proton source.

$$-d[e^-_{am}]/dt = k_{obs}[e^-_{am}]^2[\text{ketone}][\text{Na}^+] \qquad (6)$$

The results of this study and the above conclusions lead us to propose the mechanism (7)—(14) for the sodium–ammonia reduction of the non-enolizable ketone TMP.

$$R_2CO + e^-_{am} \rightleftharpoons R_2CO^{-\cdot} \qquad (7)$$

$$R_2CO^{-\cdot} + Na^+ \rightleftharpoons Na^+|R_2CO^{-\cdot}\ (\text{ion pair}) \qquad (8)$$

$$Na^+|R_2CO^{-\cdot} + e^-_{am} \longrightarrow Na^+|R_2CO^{2-} \qquad (9)$$

In the absence of an added proton donor reactions (10) and (11) occur. The net reaction in the absence of a proton donor is (12).

$$Na^+R_2CO^{2-} + NH_3 \longrightarrow R_2CHO^- + NH_2{}^- + Na^+ \qquad (10)$$

$$R_2CO + NH_2{}^- \longrightarrow R_2C(NH_2)O^- \qquad (11)$$

$$2R_2CO + 2e^-_{am} + NH_3 \longrightarrow R_2CHO^- + R_2C(NH_2)O^- \qquad (12)$$

In the presence of an added proton donor we have reaction (13). The net reaction in the presence of an added proton donor is (14).

$$R_2CO^{2-}|Na^+ + R'OH \longrightarrow R_2CHO^- + R'O \qquad (13)$$

$$R_2CO + 2e^-_{am} + R'OH \longrightarrow R_2CHO^- + R'O^- \qquad (14)$$

If formation of the dianion (9) is the rate-determining step, the rate law (15) is obtained.

$$-\frac{d[e^-_{am}]}{dt} = 2\frac{k_7k_8}{k_{-7}k_{-8}}k_9[e^-_{am}]^2[\text{ketone}][\text{Na}^+] \qquad (15)$$

Our proposed mechanism is consistent with the observed fourth-order kinetics and can account for the dependence of the rate constant on the sodium cation concentration. The ion-pairing of the ketyl radical anion is deemed necessary to reduce the charge–charge repulsion of negative charges on adjacent atoms in the formation of a vicinal dianion ion-pair [equation (9)]. Protonation is suggested to occur after formation of the dianion ion-pair, in agreement with the observations that an added proton source had no effect on the observed reaction rate while added 2,2,2-cryptand markedly decreased the rate. The independence of the rate from an added proton source is strong support for an e$^-$, e$^-$, H$^+$ pathway.[1] It should be noted that, in a previous study, we found an identical rate law for the Na–NH$_3$ reduction of DMF and DMA.[8]

An alternative mechanism, which can also account for the observed rate law, comprises reactions (16) and (17). The product of reaction (16) is consistent with a spin-paired species (metal anion or ionic aggregate) which has received considerable attention.[17–19] The present study cannot distinguish between reactions (7)—(9) and reactions (16) and (17). However, the fact that ketyl radical anions have been observed[7,20,21] is not consistent with a mechanism involving reactions (16) and (17). House[3] based his suggested mechanism in part on the observation that the reduction potentials of the alkali-metals do not appear to be sufficient to add a second electron to an aliphatic radical anion. Moreover, benzophenone has been shown to undergo two distinct single-electron transfers by both sodium–ammonia reduction[22] and cyclic voltammetry studies[23] in liquid ammonia. Although benzophenone has traditionally been treated as a mechanistic special case in that both a stable radical anion and dianion can be formed, we suggest that benzophenone is probably not a special case since two single-electron transfers in the reduction of TMP can readily account for the observed kinetic data.

$$Na^+ + 2e^-_{am} \rightleftharpoons Na^- \qquad (16)$$

$$Na^- + R_2CO \longrightarrow R_2CO^{2-}/Na^+ \qquad (17)$$

In the present study, the 1:1 stoicheiometry (mol Na:mol ketone) observed in the absence of a proton donor is consistent with that observed for the reaction of another non-enolizable ketone, 2,2,6,6-tetramethylcyclohexanone, with lithium in liquid ammonia.[24] Enolizable, aliphatic ketones are known to be reduced according to a 1:1 stoicheiometry under these conditions.[16,24,25] It is also known that an equimolar mixture of the alcoholate and the enolate is rapidly produced with no further reduction of the enolate.[26] In order to explain the observed 1:1 stoicheiometry (Tables 1 and 2), we propose that a stable amino:alkoxide, similar to that suggested by Bellamy *et al.*,[24] is formed [equation (11)]. Upon acidification of the products, equal molar amounts of the alcohol and original ketone were recovered (Table 2). Also, Nessler's reagent confirmed the presence of ammonia after acidification of the dried evacuated salts. Moreover, addition of $LiNH_2$ to the ketone solution prior to treatment with $Na–NH_3$ resulted in no reaction involving the ammoniated electron.

When an added proton donor (EtOH or H_2O) was present, a 2:1 stoicheiometry was observed resulting in a high yield of the alcohol (Tables 1 and 2). The results of the present study with a non-enolizable ketone suggest that an added proton donor prevents formation of an amino:alkoxide [equation (11)]. The necessity of a proton donor in the metal–NH_3 reductions of both enolizable and non-enolizable ketones cannot be overemphasized.[1] In addition, the use of NH_2^- as a blocking reagent in both electrochemical and dissolved metal reductions of the carbonyl group warrants further investigation.

The intermediate detected during the reaction of TMP with sodium is tentatively assigned as the TMP radical anion or its ion pair. This assignment is consistent with our observation of the intermediate even when alcohol was present in the reaction mixture. A dianion would not be expected to be long-lived enough for detection under our experimental conditions. Simultaneous optical absorption–e.s.r. measurements using a continuous reactor, such as the apparatus employed by Kemp,[27] would be helpful in clarifying this assignment. If the observed intermediate is indeed the radical anion (or an ketyl ion-pair), then the slow decay of the red-black colour (seen most distinctly when TMP was used in great excess) can be explained in terms of the equilibria between the ammoniated electron, the ketyl, and the metal ketyl [equations (7) and (8)]. A small, steady-state concentration of ammoniated electron, present in concentrations below our detection limit of 10^{-5}M, can account for the observed lifetime of this intermediate. Moreover, these equilibria explain dianion formation of TMP even when the ammoniated electron is used as the limiting reagent.

In summary, the sodium–ammonia reduction of a non-enolizable ketone was found to obey a fourth-order rate law, second order with respect to e_{am}^-, first order with respect to the ketone, and first order with respect to the sodium cation. The addition of a proton donor (ethanol) had no effect on the observed rate constant. The amide ion has been found to be an effective blocking agent for the carbonyl group in dissolved metal reductions. Finally, the results of the present study are consistent with a dianion mechanism for the dissolved metal reduction of a non-enolizable ketone, but extension of such a mechanism to aliphatic, enolizable ketones cannot be made without further study.

Acknowledgements

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