This is to be expected, since the log $(i_d - i)/i$ vs. E plot for the H_2O_2 wave is not a straight line either, indicating an α which is potential dependent. The α's obtained from both plots are *ca.* 0.2 (assuming $n = 1$).

In order to avoid the uncertainty in the value of α, it is preferable to employ the above equations to predict the relative values of i/i_d at the *same* potential in the various borate solutions. At the same potentials, and hence the same k_e, it follows from equations 10 and 11 that over the entire range of borate concentrations

$$(1/i - 1/i_d)\,KC/(K + (B)) = \text{const.} \qquad (13)$$

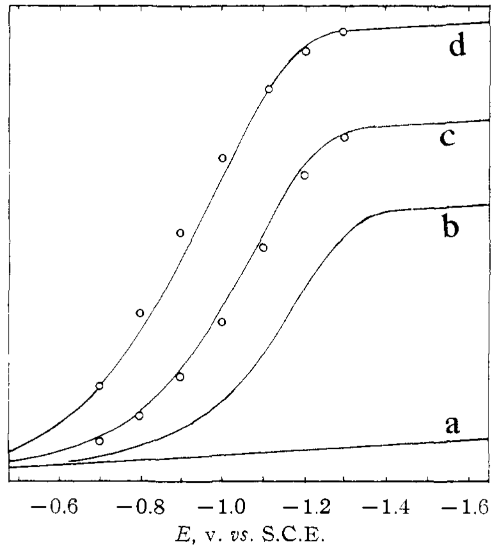

Fig. 4.—Current voltage curves of H_2O_2 of approx. the same concentration in borate solutions of $\mu = 0.5$: a, residual current; b, 0.44 M borate; c, 0.123 M borate; d, no borate. The circles are points calculated on the basis of curve b and eq. 13.

To test this equation polarograms were run in *ca.* 0.5 millimolar H_2O_2 solutions containing 0, 0.123 and 0.44 M sodium borate plus sufficient sodium nitrate to bring the ionic strength up to 0.5. A cell of very low resistance was used. With the wave at 0.44 M borate as a basis, those at the other two concentrations were constructed by the application of equation 13, using K values obtained from Fig. 1. The calculated points in Fig. 4 are seen to agree quite satisfactorily with the tracings of the recorded waves.

This agreement does not imply that equation 2 gives a correct picture of the perborate equilibrium, since the experimental values of K were used, which vary with the borate concentration. When a constant value $K = 0.030$ was used, agreement was poorer. However the agreement does show that the equilibrium observed between H_2O_2 and perborate in the bulk of the solution by means of E_c measurements also exists at the drop surface at the rising portion of the wave, and supports a reduction mechanism which is first order with respect to H_2O_2, as assumed in equation 10.

Acknowledgment.—The author wishes to express his gratitude to the Research Corporation for financial assistance which made this investigation possible.

HANOVER, N. H.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Potentiometric Titrations in Liquid Ammonia. IX. Reduction of Iodides of Zinc, Cadmium and Mercury[1]

BY GEORGE W. WATT AND PHILIP S. GENTILE

RECEIVED JUNE 30, 1955

Potentiometric titration of the iodides of zinc(II), cadmium(II) and mercury(II) with potassium in liquid ammonia shows only the reduction to the corresponding elemental metals and provides no evidence for the intermediation of the +1 oxidation states of these metals. From related titrations involving higher ratios of reductant to salt, evidence for the formation of the intermetallic compounds KCd_3, KHg and KHg_2 was obtained. The anticipated KZn_4 was not detected.

Earlier publications from this Laboratory have illustrated the use of potentiometric titration data in the interpretation of the reactions that occur between salts and solutions of alkali metals or alkali metal amides in liquid ammonia. For example, these techniques have been used to establish the identity of the sulfides that are formed when the polysulfides of the alkali metals are titrated with standard solutions of these metals.[2] Similarly, the titration of potassium tetracyanonickelate (II) and potassium hexacyanocobaltate (III) with ammonia solutions of potassium has provided information relative to the mechanism of these reduction reactions as well as evidence for the +1 oxidation state of cobalt.[3]

Recent reports of evidence possibly indicative of the +1 oxidation states of magnesium[4] and calcium[5,6] prompt us to report in this paper our earlier efforts to detect the +1 oxidation states of zinc, cadmium and mercury by the potentiometric titration of the corresponding iodides with solutions of potassium in liquid ammonia.

The literature provides no convincing evidence for the +1 oxidation state of zinc, although there

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[1] This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.

[2] G. W. Watt and J. B. Otto, Jr., *J. Electrochem. Soc.*, **98**, 1 (1951).

[3] G. W. Watt, J. L. Hall, G. R. Choppin and P. S. Gentile, THIS JOURNAL, **76**, 373 (1954).

[4] R. L. Petty, A. W. Davidson and J. Kleinberg, *ibid.*, **76**, 363 (1954).

[5] P. Ehrlich and L. Gentsch, *Naturwissenschaften*, **40**, 460 (1953).

[6] G. Wehner, *Z. anorg. allgem. Chem.*, **276**, 72 (1954).

have been numerous reports of compounds of cadmium(I). Hollens and Spenser,[7] however, have re-examined the latter case and have reached the conclusion that the substances in question do not involve Cd^{1+}. Although compounds of Hg^{1+} are said to disproportionate in liquid ammonia,[8] the possibility of detection of the transitory existence of this species is not precluded.

It should also be recognized that even if the primary or secondary reactions in the reduction of the iodides of zinc, cadmium and mercury should produce the elemental metals, extension of the titrations should provide evidence for the formation of specific intermetallic compounds of potassium and the Group II metals.

Experimental

All materials employed in this work were reagent grade chemicals and all titrations were carried out under strictly anhydrous conditions in an oxygen-free atmosphere. Unless otherwise indicated the reference electrode used was of the difference-indicator type[9] and the procedures were the same as those previously described.[2] The initial volume of each solution titrated was approximately 50 ml.

Zinc(II) Iodide.—In a typical experiment, 0.4643 g. of zinc(II) iodide together with 0.10 g. of potassium iodide (as a supporting electrolyte) was titrated with 0.1230 *N* potassium solution over a period of 15 hr. (Fig. 1). A black precipitate formed upon addition of the first increment of titrant and continued to form until 25.1 ml. had been added, whereupon the blue color characteristic of an ammonia solution of a metal persisted for >9 hr. A sample of the black ammonia-insoluble reduction product gave an X-ray diffraction pattern[10] which led to interplanar spacings and relative intensities all of which correspond to those previously recorded[11] for elemental zinc and zinc(II) oxide; the latter was presumably present owing to partial oxidation during transfer of the sample to the capillary tube.

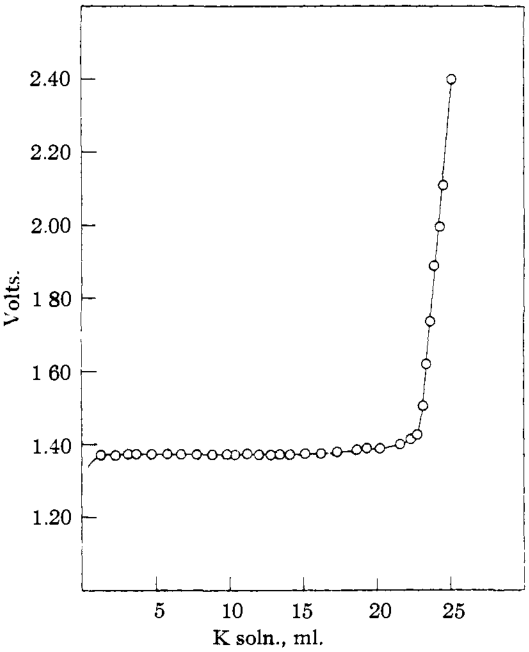

Fig. 1.—Potentiometric titration: ZnI$_2$ with K.

Cadmium(II) Iodide.—In a strictly analogous manner, 0.0831 g. of cadmium(II) iodide with 0.10 g. of potassium iodide was titrated with 0.0303 *N* potassium solution over a period of 10 hr. A black precipitate formed progressively and the rate of reaction decreased markedly after addition of 15.1 ml. of titrant. As shown by Fig. 2, significant changes in potential occurred upon addition of 14.9 and 17.9 ml. of the standard potassium solution. A sample of the black ammonia-insoluble product that had been exposed to the atmosphere for a short time gave an X-ray diffraction pattern that showed the presence of elemental cadmium[11] and cadmium(II) oxide 2-hydrate[11] only.

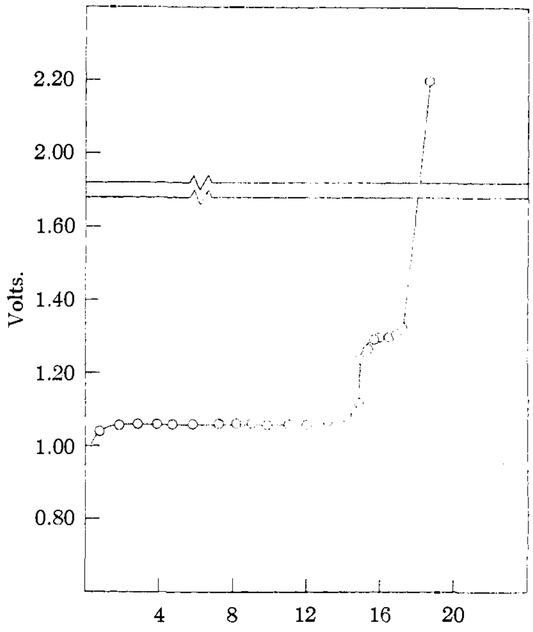

Fig. 2.—Potentiometric titration: CdI$_2$ with K.

In related experiments in which optimum conditions for intermetallic compound formation were provided, cadmium(II) iodide was reduced with excess potassium and the excess metal solution was back-titrated with standard ammonium bromide solution. Thus, ammonia was condensed upon 0.2460 g. of cadmium(II) iodide and 0.30 g. of potassium bromide, the reference electrode compartment was filled with the resulting solution, and 0.0864 g. of potassium was added to the main body of the solution. When there was no further evidence of reaction, the excess potassium was back-titrated with 0.0097 *N* ammonium bromide solution (Fig. 3); the disappearance of the characteristic blue color and a decrease in potential of the order of 1.4 v. were coincident upon addition of 21.9 ml. of titrant.

Mercury(II) Iodide.—Over a period of 9 hr., 0.1106 g. of mercury(II) iodide and 0.10 g. of potassium iodide was titrated with 0.0322 *N* potassium solution (Fig. 4). A black precipitate formed progressively and subsequently agglomerated to droplets of elemental mercury. After addition of 15.0 ml. of titrant, equilibrium potentials were not established probably owing to deposition of precipitated mercury on the indicator electrode.

When 0.0102 g. of potassium was titrated (8 hr.) with 0.0055 *N* mercury(II) iodide solution (Fig. 5), significant changes in potential occurred upon addition of 16.0 and 19.4 ml. of titrant. As the first end-point was approached, a black precipitate deposited on the walls of the titration cell; this solid then reacted to form a yellow-green solution at the second end-point. Further additions of a large excess of titrant produced a bright yellow precipitate that subsequently proved to be insoluble in and unreactive toward a liquid ammonia solution of ammonium iodide, and stable when exposed to the atmosphere or to water at room temperature. This product, which apparently results from the reaction between KHg$_2$ and HgI$_2$ was not further investigated.

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(7) W. R. A. Hollens and J. F. Spenser, *J. Chem. Soc.*, 1062 (1934); 459 (1935).

(8) H. A. Laitinen and C. E. Shoemaker, THIS JOURNAL, **72**, 663 (1950).

(9) G. W. Watt and D. M. Sowards, *J. Electrochem. Soc.*, **102**, 46 (1955).

(10) Obtained using Cu Kα radiation, a Ni filter, 30 kv. tube voltage, 15 ma. filament current, and an exposure time of 4 hr.

(11) A.S.T.M. Index of X-ray Diffraction Patterns, Supplementary Set 1, Philadelphia, Pa., 1945.

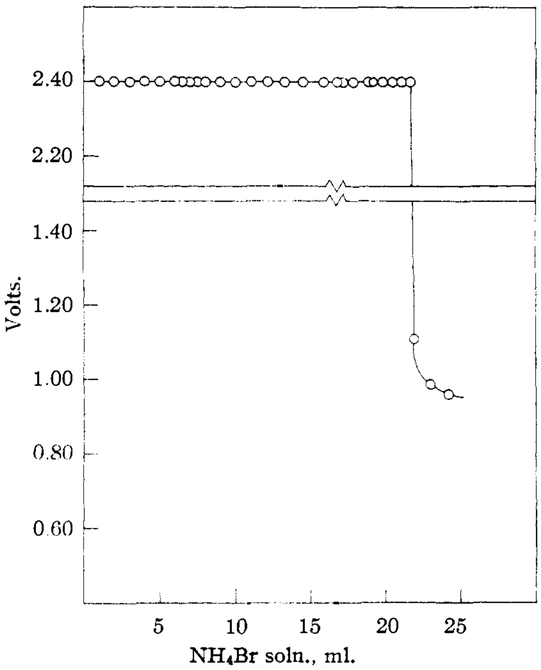

Fig. 3.—Potentiometric titration: CdI$_2$ + excess K, with NH$_4$Br.

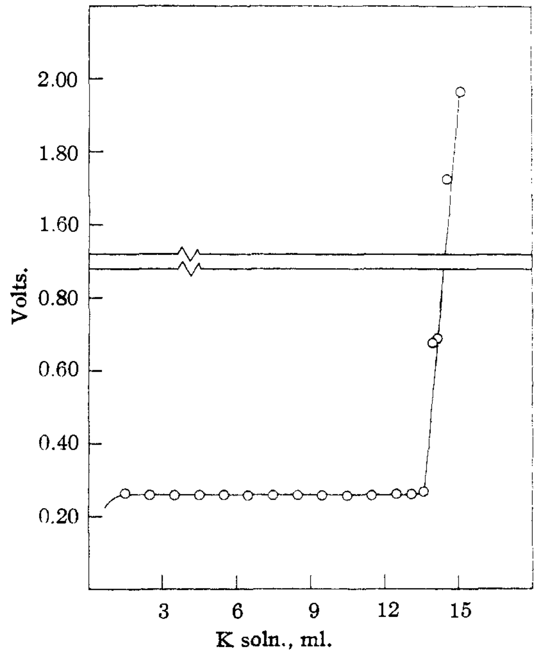

Fig. 4.—Potentiometric titration: HgI$_2$ with K.

In a back-titration similar to that described above, 0.1535 g. of mercury(II) iodide and 0.10 g. of potassium iodide was treated with excess potassium (0.0451 g.) and then back-titrated with 0.0017 *N* ammonium iodide solution. A mercury-saturated mercury(II) chloride reference electrode[12] was used in this titration. After 7.8 ml. of the latter solution had been added, a sharp decrease in potential of >1 v. occurred, the blue color was discharged, and the presence of a finely divided black precipitate became evident. The equivalence point corresponding to the formation of KHg is 7.8 ml. Further addition of titrant produced no significant changes in potential; the black precipitate dissolved and the solution was colorless after addition of 20.0 ml. Elemental mercury was not precipitated.

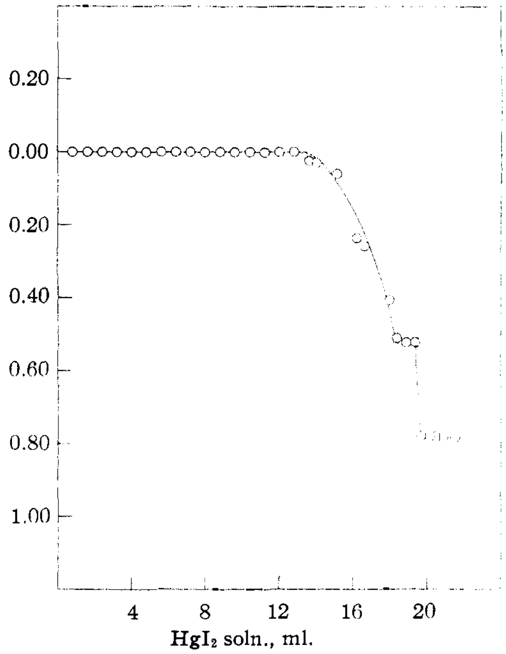

Fig. 5.—Potentiometric titration: K with HgI$_2$.

Discussion

The data of Fig. 1 show no change in potential corresponding to the volume of potassium solution (11.8 ml.) calculated for the 1-electron reduction of Zn^{2+} to Zn^{1+}. This fact, together with the visual observations, the change in potential upon addition of 23.9 ml. (calcd., 23.6 ml.), and the identification of elemental zinc, show that the primary reaction is the 2-electron reduction of Zn^{2+} to Zn°. Within experimental error the observed end-point could equally well be attributed to the formation of KZn_{12} (calcd., 24.4 ml.), but this product is ruled out by the X-ray diffraction data. Both KZn_{12} and KZn_4 were to be anticipated by analogy to earlier studies on the reduction of zinc(II) iodide with sodium in ammonia. Zintl and co-workers[13] reported that the potentiometric titration of the iodide with sodium solution gave evidence for the formation of $NaZn_{12}$, but earlier work by Kraus and Kurtz[14] failed to detect $NaZn_{12}$ and provided apparently conclusive evidence for the formation of $NaZn_4$ which was later confirmed by Burgess and Rose.[15] Although the possibility of specific chemical differences between liquid ammonia solutions of sodium and potassium cannot be discounted entirely,[16] the product reported by Zintl, *et al.*, was probably Zn° rather than $NaZn_{12}$. In the present experiments, the formation of KZn_4 would have required addition of 26.5 ml. of potassium solution whereas the blue color indicative of unreacted metal solution persisted for many hours after addition of 25.1 ml.

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[12] G. W. Watt and D. M. Sowards, *J. Electrochem. Soc.*, **102**, 545 (1955).

[13] E. Zintl, J. Goubeau and W. Dullenkopf, *Z. physik. Chem.*, **A154**, 1 (1931).

[14] C. A. Kraus and H. F. Kurtz, THIS JOURNAL, **47**, 43 (1925).

[15] W. M. Burgess and A. Rose, *ibid.*, **51**, 2127 (1929).

[16] C. W. Keenan and W. J. McDowell, *ibid.*, **75**, 6348 (1953).

It is believed that our failure to detect KZn_4 is attributable to the very slow rate of reaction between zinc and potassium owing to the low concentrations of potassium solutions employed. Both Kraus and Kurtz and Burgess and Rose used much more concentrated metal solutions.

Figure 2 shows that cadmium(II) iodide is reduced directly to elemental cadmium (calcd., 14.9 ml.; found, 15.0 ml.) which was confirmed by X-ray diffraction patterns. If this reaction proceeds through the intermediation of Cd^{1+}, this species is not detectable by the method used. The slow secondary reaction shown by Fig. 2 apparently leads to the formation of KCd_3 (calcd., 17.5 ml.; found, 17.9 ml.), which was confirmed by the back-titration method illustrated by Fig. 3 (calcd. for KCd_3, 22.2 ml.; found, 21.9 ml.). These and several related titrations that employed modified procedures (but which are not reported in this paper) provided no evidence whatever for the compounds KCd_7 and KCd_{11} previously reported.[17]

Although the titration of mercury(II) iodide with potassium (Fig. 4) shows only the 2-electron reduction to elemental mercury (calcd., 15.1 ml.; found, 14.5 ml.), which was confirmed by the identification of this product, the titration of potassium with mercury(II) iodide solution (Fig. 5) gives evidence of the formation of KHg (calcd., 15.8 ml.) and KHg_2 (calcd., 19.6 ml.), both of which are known compounds.[18] Further confirmation of the formation of KHg, but not KHg_2, was obtained from the experiments in which mercury(II) iodide was reduced with excess potassium followed by back-titration with ammonium iodide solution. In these cases, as well as in titrations involving the reduction of cadmium(II) iodide, it was observed that the identity of the specific intermetallic compounds detected is quite sensitive to the conditions prevailing, particularly concentration. In order to obtain reproducible stoichiometry, it is necessary to control all conditions within a rather narrow range.

AUSTIN, TEXAS

[17] D. T. Smith, *Z. anorg. Chem.*, **56**, 119 (1908).

[18] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., New York, N. Y., 1923, p. 1015.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Structure and Reactivity in the Vapor Phase Photolysis of Ketones. II. Methyl Neopentyl Ketone[1]

BY T. W. MARTIN AND J. N. PITTS, JR.[2]

RECEIVED JUNE 2, 1955

The major products of the vapor phase photolysis of $MeCOCH_2CMe_3$ from 120 to 250° at 3130 and 2654 Å. are isobutylene and acetone in amounts that are nearly equivalent, and virtually independent of temperature and wave length. The quantum yield, Φ, of isobutylene at 3130 Å. is 0.23 and 0.27 at 120 and 250°, respectively. Φ_{CO} under the same conditions increases from 0.04 to 0.17. Other minor non-condensable products are CH_4, C_2H_6, Me_3CH and Me_4C. A mechanism is proposed in which the major products arise directly from a primary intramolecular process, whereas the minor products come from secondary thermal reactions of radicals formed in several free radical primary processes. $MeCOCH_2CHMe_2$ also photodissociates chiefly into acetone and an olefin, in this case propylene. It is proposed that this type of process is general for aliphatic ketones having γ-hydrogen atoms and that the efficiency of the process can be correlated with the structure of the ketone and its characteristic mass spectrometric cracking pattern.

Although all aliphatic ketones photodissociate to some extent by free radical processes, evidence has accumulated that the more complex ketones having alkyl groups with γ-hydrogens also react to a significant degree by a concerted intramolecular rearrangement that gives an olefin and a lower ketone.[3,4] For example, it is now well established that methyl *n*-butyl ketone photodissociates to a large extent by this type of process into acetone and propylene.[5,6]

A major purpose of the present research was to irradiate methyl neopentyl ketone under a variety of conditions and determine the effect a large, highly branched, alkyl group with many primary γ-hydrogens might have on the efficiency of this rearrangement.

Experimental

Photolyses were carried out in a cylindrical quartz cell having an outside diameter of 3.0 cm. and a volume of 123 cc. The light source, a medium pressure mercury arc, Hanovia Type 73A, was operated at approximately 4.3 amp. and 145 v. A.C. It gave essentially constant intensities at both 2654 and 3130 Å. The lamp was mounted in a water-cooled housing attached directly to a Farrand Model 300 UV monochromator. A quartz lens, two inches in diameter with a six inch focal length, served to fill the reaction cell with collimated light.

Relative intensities were obtained by means of an RCA-935 phototube operated on a 180 volt battery power supply. The phototube current was measured with a No. 10-210 American Instrument Co. "Microphotometer." This instrument is designed primarily for use with a photomultiplier tube but was adapted for the 935 tube by connecting the anode of the 935 to pin 10 of the photomultiplier socket in the input lead of the "Microphotometer." A variable 5 megohm shunt in parallel with the "Microphotometer" was employed to extend the range of the instrument to large phototube currents. Acetone at 120° was used as an internal actinometer, with Φ_{CO} assumed to be unity at both 3130 and 2654 Å. The reaction cell was placed in an aluminum block furnace controlled by a Brown potentiometer. Methyl

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[1] From the Ph.D. Dissertation of T. W. Martin, Northwestern University, 1954. (b) Presented in part at the Conference on Photochemistry and Free Radicals, University of Rochester, September, 1954.

[2] Division of Physical Sciences, University of California, Riverside, California.

[3] A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

[4] C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

[5] R. G. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934).

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