chain termination step although at least one such step is known to be present since the molecular weight of the product does not increase indefinitely with the amount of olefin polymerized. The presence of such a step (provided there is no appreciable amount of catalyst destruction) would have no observable effect on the results of the present kinetic study.

Summary

1. The kinetics of the polymerization of propylene by means of aluminum bromide in the presence of hydrogen bromide promoter have been investigated.

2. A mechanism which accounts for the experimental data has been proposed.

3. Approximate values of a rate constant, an equilibrium constant and the corresponding activation and heat energies have been determined.

4. The heat of polymerization of propylene has been found to be approximately 16.5 kcal. per mole.

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

Molybdenum(III) Oxide[1]

BY GEORGE W. WATT AND DARWIN D. DAVIES[2]

Although several methods for the formation of molybdenum(III) oxide hydrates have been described,[3] there is no satisfactory procedure for the direct production of the anhydrous oxide. The method of Wherry and Smith[4] yields pure molybdenum(II) oxide 3-hydrate; the same product in less pure form is afforded by the method of Berzelius.[5]

In the course of certain work on the reduction of molybdenum(VI) oxide by means of solutions of potassium in liquid ammonia, it has been found that anhydrous molybdenum(III) oxide may be formed in accordance with the equation

$$2MoO_3 + 6K + 3NH_3 \longrightarrow Mo_2O_3 + 3KOH + 3KNH_2$$

Upon completion of the reduction reaction, the oxide is purified by treatment with ammonium bromide followed by washing with liquid ammonia at least ten times. Experiments described below show that the oxide thus prepared and purified forms a 3-hydrate identical with that prepared by the method of Wherry and Smith.[4] In the course of this work it was shown also that commercial products purported to be molybdenum(III) oxide consist principally of molybdenum(IV) oxide and molybdenum.

Experimental

Materials.—Molybdenum(VI) oxide was prepared as described previously.[6] Samples prepared by different methods and treated differently prior to use gave identical results. All of the other chemicals employed were of reagent grade.

Methods.—Equipment and procedures for the conduct of the reduction reactions in liquid ammonia at its normal boiling point and under anhydrous conditions were essentially identical with those described by Watt and Moore.[7]

Preparation of Molybdenum(III) Oxide.—Small samples of molybdenum(VI) oxide (0.3–0.7 g.) in 20–25 ml. of anhydrous liquid ammonia[8] were reduced by addition of quantities of potassium slightly in excess of 3 equivalents. Typical data relative to these reactions are given in Table I. That the reduction is substantially quantita-

TABLE I

PREPARATION OF MOLYBDENUM(III) OXIDE

MoO_3, g.	K g.	K equiv.	H_2, cc. at 0°, 760 mm.	NH_4Br, g.	Ratio[a] K/ MoO_3	Mo,[b] %
0.5205	0.4430	3.13	5.5	None	3.00	78.85
.5250	.4425	3.10	4.2	None	3.00	78.78
.6522	.5511	3.11	5.6	0.6200	2.99	79.82
.5650	.4720	3.08	2.9	.5120	3.01	79.90
.6006[c]	.5131	3.15	7.2	.5080	2.99	79.83
.4999[c]	.4281	3.15	3.0	1.0021	3.08	79.71

[a] Calculated in terms of molybdenum(VI) oxide used and the total potassium added less that equivalent to the quantity of hydrogen collected. [b] Calcd. for Mo_2O_3: Mo, 79.99. In addition to analyses for molybdenum, each insoluble product was analyzed for nitrogen and potassium. For runs in which ammonium bromide was not added, the results were: N, 0.72 ± 0.03; K, 2.99 ± 0.16. When ammonium bromide was added, the results were: N, 0.52 ± 0.09; K, 0.58 ± 0.08. These data reflect the improvement in purity resulting from treatment with ammonium bromide, but show also that this treatment together with at least 10 washings with liquid ammonia fails to remove these impurities completely. The analytical values for molybdenum bespeak a degree of purity that is incompatible with the analytical values for nitrogen and potassium. However, the method employed in analyses for molybdenum was carefully checked using samples of known purity and it is believed that the molybdenum analyses are the most reliable. Also, there were present in the molybdenum(III) oxide no impurities detectable by means of X-ray diffraction patterns. [c] These experiments are typical of cases in which the oxide was added to a solution of potassium, *i.e.*, a reversal of the more usual order of addition of reactants.

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(1) This work was supported in part by The University Research Institute, Project No. 25.

(2) Present address: The General Electric Co., Richland, Washington.

(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1931, Vol. XI, p. 525.

(4) Wherry and Smith, THIS JOURNAL, **29**, 806 (1907).

(5) Berzelius, *Pogg. Ann.*, **7**, 261 (1826).

(6) Watt and Davies, THIS JOURNAL, **70**, 2041 (1948).

(7) Watt and Moore, *ibid.*, **70**, 1197 (1948).

(8) Although it has been shown that molybdenum(VI) oxide reacts with liquid ammonia to form a 3-ammoniate that may be interpreted as a diammonium aquoammonomolybdate,[6] its behavior upon reduction with potassium is not typical of ammonium salts. The molecular hydrogen liberated during the course of the reduction reactions was only that equivalent to the excess potassium added.

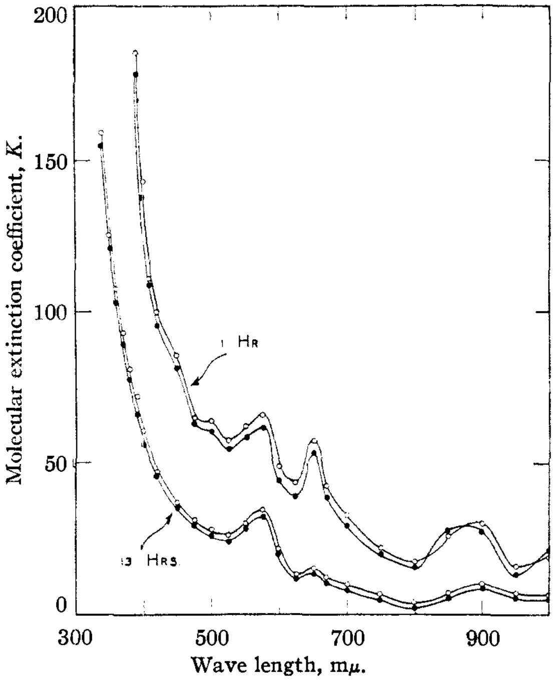

Fig. 1.—○, Product by method of Wherry and Smith; ●, product from liquid ammonia.

tive is indicated by the fact that the ammonia-soluble fractions gave negative qualitative tests for molybdenum, and supported by the reaction ratios and analytical data for molybdenum as listed in Table I.

Properties of Molybdenum(III) Oxide.—Prepared as described above, anhydrous molybdenum(III) oxide is a very finely divided black solid, d^{25}_4 7.07. The oxide dissolves readily in 6*N* hydrochloric acid solution to form a solution having a distinctive purple-red color, the intensity of which decreases progressively (probably owing to atmospheric oxidation) over a period of several hours to a permanent pale pink color. When heated for three hours at 325° in an atmosphere of dry carbon dioxide, the black oxide is converted without change in weight or molybdenum content to a form having a color quite like that of potassium permanganate crystals. A sample of the anhydrous oxide was converted to molybdenum(III) oxide 3-hydrate by agitation with water for fifteen minutes at 25°. The insoluble black solid was filtered and dried *in vacuo* over concentrated sulfuric acid for twenty-four hours.

Anal. Calcd. for $Mo_2O_3 \cdot 3H_2O$: H_2O, 18.36. Found: H_2O, 18.20.

Neither the original black oxide, the heat-treated oxide, nor the 3-hydrate gave an X-ray diffraction pattern during twelve-hour exposures to Cu K_α radiation when samples were mounted in thin-walled Pyrex capillary tubes. Samples mounted on glyptal underwent oxidation during the exposures and the resulting diffraction patterns consisted exclusively of the lines characteristic of molybdenum (IV) oxide.[9]

For comparison, molybdenum (III) oxide 3-hydrate was prepared by the following modification of the method of Wherry and Smith.[4] In a typical case, 0.1200 g. of molybdenum(VI) oxide was dissolved in 15 ml. of 26% aqueous ammonia, made acidic to methyl orange by addition of 10% sulfuric acid solution and electrolyzed for two hours with a current of 5 amp. at 16 v. in a 30-ml. platinum crucible cathode (rotating platinum spiral anode).

Anal. Calcd. for $Mo_2O_3 \cdot 3H_2O$: H_2O, 18.36. Found: H_2O, 18.30.

Following dehydration, the anhydrous oxide was analyzed for molybdenum.

Anal. Calcd. for Mo_2O_3: Mo, 79.99. Found: Mo, 79.92.

The reduction was quantitative and the resulting 3-hydrate exhibited properties identical in all respects with those of that prepared from the anhydrous oxide formed in liquid ammonia. The identity of these two products was further substantiated by the absorption spectra shown in Fig. 1, which shows that the initial and final spectra and the rate of change are essentially the same. The solutions employed were 0.002 *M* with respect to molybdenum and 6 *M* in hydrochloric acid.

Commercial Molybdenum(III) Oxides.—Failure of any of our samples to give an X-ray diffraction pattern was surprising in view of the fact that diffraction data for the oxide in question had been reported.[9] Since we were unable to get a diffraction pattern using samples prepared by any of the available methods, samples of commercial molybdenum "sesquioxide" were examined. One such sample was a black solid that was ***insoluble*** in 6*N* hydrochloric acid solution.

Anal. Calcd. for $Mo_2O_3 \cdot 3H_2O$: Mo, 65.28. Found: Mo, 77.25.

This material in Pyrex capillary tubes gave X-ray diffraction patterns consisting of the lines characteristic of molybdenum(IV) oxide and molybdenum.[9] It was learned subsequently[10] that the data previously published[9] were obtained using a commercial product of the same origin and that the authors of the original paper were aware of the discrepancy prior to the present work.

A sample from a different source and prepared[11] by the method of Berzelius[5] consisted of a partially hydrated black solid that was sufficiently soluble to impart only a faint coloration to 6*N* hydrochloric acid solution.

Anal. Calcd. for $Mo_2O_3 \cdot 3H_2O$: Mo, 65.28. Found: Mo, 70.08.

This product gave no X-ray diffraction pattern, but after complete dehydration at 325° in a non-oxidizing atmosphere samples in Pyrex capillary tubes gave a pattern all lines in which could be accounted for in terms of the known lines characteristic of molybdenum and molybdenum(IV) oxide.[9]

Summary

1. The reduction of molybdenum(VI) oxide with three equivalents of potassium in liquid ammonia at −33.5° has been shown to result in anhydrous molybdenum(III) oxide.

2. The anhydrous oxide has been shown to form a 3-hydrate that is identical with the corresponding compound formed by an independent method.

3. Commercial products alleged to be molybdenum(III) have been shown to consist of mixtures containing little if any of this oxide.

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[9] Hanawalt, Rinn and Frevel, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 457 (1938).

[10] Rinn, private communication.

[11] Keller, private communication.