Differential Thermal Analysis Study of the Reduction of Cobalt Oxide, Iron Oxide, and Copper Oxide

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Differential thermal analysis (DTA) studies of cobalto-cobaltic oxide, alpha-ferric oxide, and cupric oxide were made in flowing hydrogen (5000 space velocity) from 20° to 1000° C. at a programming rate of approximately 5° to 6° C. per minute. Partial runs were stopped after individual peaks to afford a better correlation between reduction and the exotherms and endotherms. Approximately one-half of the cobalto-cobaltic oxide was reduced at 265° C. At 375° C., there remained 40 to 50% cobaltous oxide with the alpha-cobalt. Reduction was complete at 495° C. The reduction of alpha-ferric oxide to ferroso-ferric oxide was approximately one-half complete at 320° C. and essentially complete at 380° C. Reduction to 635° C. gave 50 to 70% alpha-iron, and complete reduction to alpha-iron was found at 760° C. The DTA pattern showed reversible structural changes of iron at 775° and 925° C. Reduction of copper oxide was 90 to 97% complete at 250° C. No heat effects were observed above 350° C.

REDUCTION of the oxides of cobalt, iron, nickel, and copper have important roles in catalyst manufacture and application. Crystallite size, per cent reduction, intermediate compound formation, and many other physical and chemical properties are frequently related to the temperature and time of reduction. The increasing and varied demand on catalyst performance requires a basic understanding of the physical and chemical properties.

Pure cobalt oxide or cobalt oxide hydrate can be reduced in hydrogen very readily at temperatures at least as low as 300° C. (*2*). The apparent activation energy of the cobalto-cobaltic oxide reduction has been reported to be about 17.8 kcal. (*5*).

Studies show that the reduction of ferric oxide at 435° C. is very slow, requiring 96 hours to obtain iron free from ferrous oxide (*7*). For ferric oxide, which has been largely reduced to magnetite, a new period occurs where reduction rate is accelerated (*6*).

Curves of the rate of reduction of copper oxide as a function of the time were determined at 201° C. in a static system for samples prepared in various manners (*8*). Differential thermal analysis study of the reduction of nickel oxide indicated the transition of nickel oxide from a slightly distorted (rhombohedral) variant of the rock salt structure to the rock salt structure. The reversibility of the phase transition at 250° C. was demonstrated. Reduction of nickel oxide was related to the 250° to 400° C. exotherm. Observation of a reversible transition of α- to β-nickel at 360° C. was made. No heat effects were detected above 400° C. (*3*).

This report is concerned with a differential thermal analysis (DTA) study of the oxides of cobalt, iron, and copper in hydrogen from 20° to 1000° C. at a programming rate of approximately 5° to 6° C. per minute. X-ray diffraction studies were made to understand better the significance of each DTA peak.

APPARATUS AND TECHNIQUE

The R.L. Stone differential thermal analysis equipment, Model DTA-10MC, was used for reductions. Temperature was programmed at 5° to 6° C. per minute up to 1000° C. for a complete run or to an intermediate temperature for a partial run. A water-cooled-type furnace surrounds the sample holder. A large dome is placed over the furnace for controlled atmosphere work. The sample (0.2 to 0.3 cc., <400 mesh) and a comparison material (α-alumina, prepared by calcining Filtrol hydrated alumina for 24 hours at 1260° C., and confirmed by x-ray diffraction) are positioned in adjacent openings, at the upper end of gas flow tubes, located near the top of the sample head. Hydrogen is passed through the sample and the comparison material at the same rate (5000 SV). Differential temperature (Pt + 10% Rh; Pt; Pt + 10% Rh thermocouple) and reference temperature (Pt *vs.* Pt + 10% Rh thermocouple) are transmitted to different recorders. At the conclusion of each run, the sample was cooled to room temperature under hydrogen and then flushed with helium before preparation for x-ray diffraction studies.

A narrow x-ray source Geiger counter Norelco diffractometer, employing copper Kα radiation at 45 kv. and 20 ma. and cobalt Kα radiation at 45 kv. and 10 ma., was used with a rotating flat specimen holder. The sample holder is circular and slips into a rotating device located in the position occupied by the usual stationary sample holder. The sample (<400 mesh) is rotated around an axis perpendicular to the irradiated surface at approximately 80 r.p.m. The goniometer was operated at ½° per minute and the chart speed was 30 inches per hour. High precision divergence (1°) and receiving slit (0.006 inch) was used. X-ray evaluations were made using the following standard patterns (*1*): cobalto-cobaltic oxide, cobaltous oxide, α-cobalt, α-ferric oxide, ferroso-ferric oxide, ferrous oxide, α-iron, cupric oxide, and copper.

CHEMICALS

Cobalt nitrate hexahydrate (Mallinckrodt Chemical Works), iron (III) nitrate nonahydrate (Allied Chemical & Dye Corp.), and copper (II) nitrate trihydrate (Allied Chemical & Dye Corp.) met ACS specifications. Calcination of these hydrated nitrates at 649° C. for 16 hours gives, respectively, cobalto-cobaltic oxide, α-ferric oxide, and cupric oxide (confirmed by x-ray diffraction).

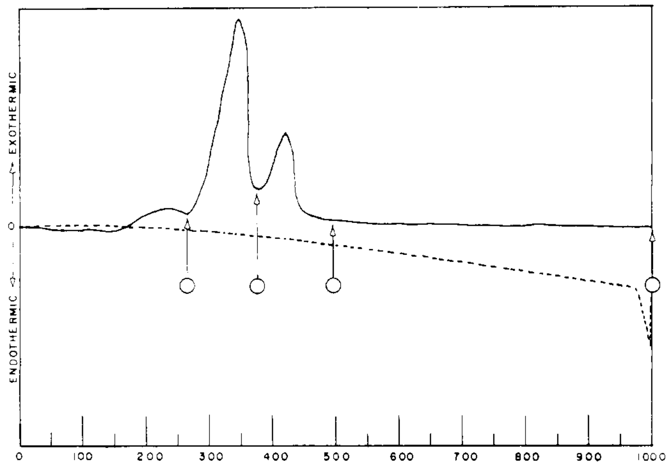

Figure 1. Reduction of cobalto-cobaltic oxide
—— Heating curve
- - - - Cooling curve
Stop points

Electrolytic hydrogen (National Cylinder Gas, 99.8% minimum purity) with all traces of oxygen removed was used for the reductions. Helium (National Cylinder Gas, 99.997% minimum purity) was employed for flushing samples before removal from DTA unit.

DISCUSSION

A complete differential thermal analysis (DTA) run (from 20° to 1000° C.) of cobalto-cobaltic oxide in hydrogen at 5000 space velocity was conducted. The mean dimension (crystallinity) of the cobalto-cobaltic oxide was greater than 1500A. Partial DTA runs in hydrogen were also made on cobalto-cobaltic oxide, stopping after each peak. These partial runs duplicated the complete run up to the temperature attained (Figure 1). The x-ray diffraction pattern of the material from the partial run to 265° C. under hydrogen, indicates 45 to 55% Co_3O_4, 5 to 10% CoO, and 35 to 45% α-Co. Approximately one-half of the cobalto-cobaltic oxide had been reduced to metallic cobalt and cobaltous oxide. The x-ray diffraction study of the partial DTA run to 375° C. shows all cobalto-cobaltic oxide being reduced, resulting in 50 to 60% α-Co and 40 to 50% CoO. For the partial DTA run to 495° C., x-ray diffraction shows only alpha-cobalt indicating complete reduction. No exothermic or endothermic reactions occurred between 495° and 1000° C. in the heating curve, nor in the entire cooling curve. The x-ray diffraction pattern for the completed run was the same as the pattern of the 495° C. partial run. Compound composition before and after each peak was reproducible.

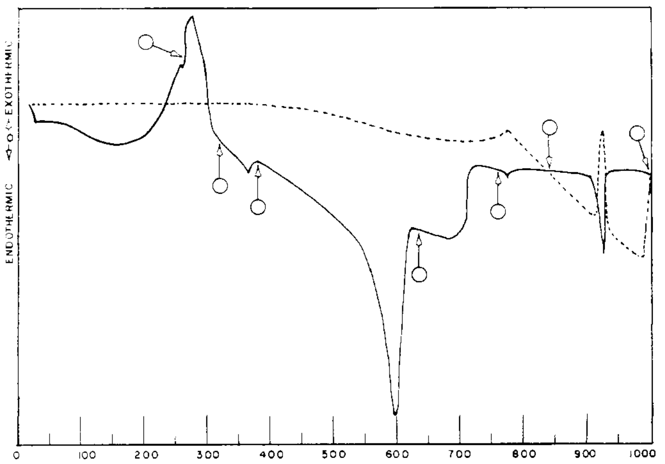

Figure 2. Reduction of alpha ferric oxide
—— Heating curve
- - - - Cooling curve
Stop points

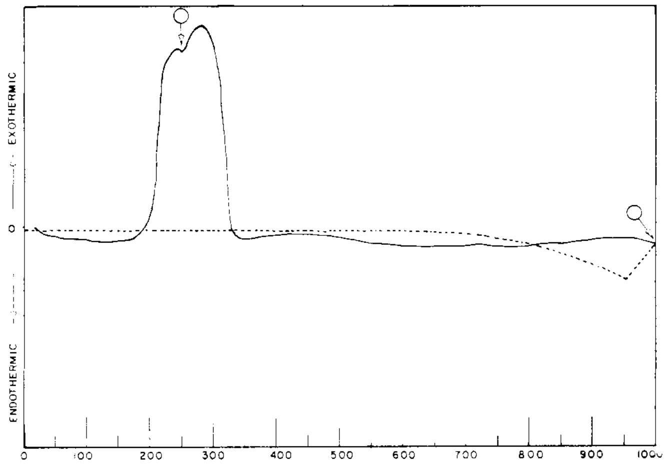

Figure 3. Reduction of copper oxide
—— Heating curve
- - - - Cooling curve
Stop points

Complete and partial DTA runs in hydrogen were made on alpha-ferric oxide having a crystallinity greater than 1500A. (Figure 2). Again, the partial runs duplicated the complete run up to the temperature attained. The run stopped at 265° C. results in a 90 to 95% α-Fe_2O_3 and 5 to 10% Fe_3O_4 mixture. Reduction to 320° C. yields 45 to 55% α-Fe_2O_3, 45 to 55% Fe_3O_4, whereas reduction to 380° C. results in 2 to 5% α-Fe_2O_3 and 95 to 98% Fe_3O_4. The small endothermic peak at 365° C. may be associated with a phase change of α-Fe_2O_3 or Fe_3O_4. Continuing the reduction to 635° C. gives 50 to 70% α-Fe, 25 to 40% Fe_3O_4, and 5 to 10% FeO. The partial DTA run to 760° C. results in 100% α-Fe, as is the case for the partial run to 840° C. and the complete run to 1000° C. The endothermic peaks at 775° and 925° C. represent

$$\alpha\text{-Fe} \xrightarrow{775^\circ\text{ C.}} \beta\text{-Fe} \xrightarrow{925^\circ\text{ C.}} \gamma\text{-Fe}$$

This is not detected by x-ray diffraction since the x-ray runs are made at room temperature, and the structural changes are reversible as is indicated by the DTA cooling curve. These structural changes agree with reported values of 760° and 908° C., respectively (*4*), rather closely considering that the runs are programmed. The run demonstrates the exothermic nature of the reduction of α-Fe_2O_3 to Fe_3O_4 and the endothermic nature of the reduction of Fe_3O_4 to α-Fe which agrees with thermodynamic calculations.

In like manner, complete and partial DTA runs in hydrogen were made on copper oxide having a crystallinity greater than 1500A. (Figure 3). As was the case in the cobalt and iron studies, the partial runs duplicated the complete run up to the temperature attained. The partial run, terminated at 250° C., results in a 90 to 97% Cu and 3 to 10% CuO mixture. The complete run shows that the reduction, as per x-ray diffraction, is complete. Reduction is more than 90% complete before the last DTA peak. No exothermic or endothermic reactions occurred between 350° and 1000° C. in the heating curve, nor in the entire cooling curve. This work indicates the absence of any copper structural changes unless such changes occur in the reduction area.

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Synthesis of Some Substituted 7-Aryl-1,2,3,4-tetrahydro-1,4-diazepin-5-ones

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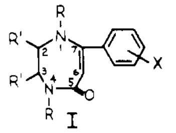
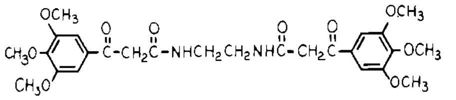
Seven 7-aryl-1,2,3,4-tetrahydro-1,4-diazepin-5-ones were prepared by the condensation of ethylenediamine with the appropriate ethyl aroylacetate. The 1,4-dimethyl- and 2,3-dimethyl-7-phenyltetrahydrodiazepinones were prepared by condensation of *N,N′*-dimethylethylenediamine and 2,3-diaminobutane with ethyl benzoylacetate. The preparation of the 3-ethyl-3,7-diphenyl analog is also described.

CONDENSATION of ethyl benzoylacetate with ethylenediamine to give 7-phenyl-1,2,3,4-tetrahydro-1,4-diazepin-5-one has been described (*2*). The present paper describes the preparation of several substituted diazepinones represented by formula I.

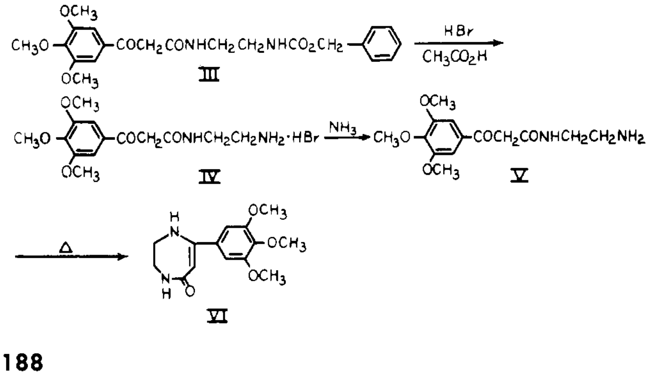


I

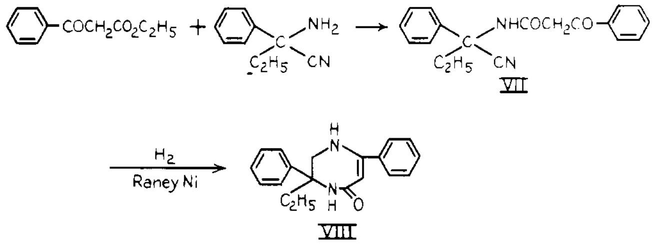


II

The 7-substituted phenyl derivatives, IX-XVI (Table I), were prepared in a manner similar to that described for the preparation of the parent compound (*2*)—i.e., condensation of an ethylenediamine with the requisite β-keto ester. This condensation, however, failed to give the desired product (VI) with ethyl 3,4,5-trimethoxybenzoylacetate, in which case the only isolable material was the linear amide II. The desired diazepinone VI was prepared as outlined below:



The 3-ethyl-3,7-diphenyl derivative VIII was prepared by the condensation of ethyl benzoylacetate with 2-amino-2-phenylbutyronitrile to give the acylated nitrile VII. Hydrogenation of VII in the presence of Raney nickel catalyst caused reductive cyclization to the desired product VIII.



The pertinent data for the diazepinones are listed in Table I.

EXPERIMENTAL

All melting points and boiling points are uncorrected.

Ethyl Benzoylacetates. The required β-keto esters were prepared by a modification of the procedure of Perkin and Weizmann (*7*) as described by Burton and Ingold (*1*). The following esters were prepared: ethyl *m*-toluoylacetate, b.p. 98-100°/0.2 mm., copper salt, m.p. 188.5-190°; ethyl *p*-chlorobenzoylacetate (*1, 10*), ethyl *m*-chlorobenzoylacetate (*4*), ethyl *p*-toluoylacetate (*6*), ethyl *p*-anisoylacetate (*9*), ethyl *m*-α,α,α-trifluoromethylbenzoylacetate (*3*), and ethyl 3,4,5-trimethoxybenzoylacetate (*5*).

7-Aryl-1,2,3,4-tetrahydro-1,4-diazepin-5-ones (Table I). The procedure used to prepare these compounds is that reported by Hofmann and Safir (*2*) for the preparation of 7-phenyl-1,2,3,4-tetrahydro-1,4-diazepin-5-one. The pertinent data are listed in Table I.