

Simple Programmed Thermoregulator

By M. W. SCOTT*, C. Y. MIN, W. A. CAMPBELL, and C. M. ANDERSON

The design and construction are described for a programmed thermoregulator which was used to provide time-temperature control in nonisothermal reaction kinetics studies of product stability. The apparatus is inexpensive to construct and provides moderate programming flexibility.

Possible applications of nonisothermal reaction kinetics in the evaluation and prediction of product stability have been under recent investigation in these laboratories. For the experimental sections of this research, a time-temperature control was required in order to obtain a constant rate of heating in the (liquid) reaction systems selected for study. A new programmed thermoregulator was designed for this purpose. The apparatus was inexpensive to construct and performed in a reliable and predictable manner. The unit also provided moderate flexibility in the types of programs which could be established.

A photograph and an assembly drawing of the programmed thermoregulator are given in Figs. 1 and 2, respectively. The construction was based on the use of a standard slide-wire type thermoregulator.¹ This was mounted on a plastic base. A synchronous motor² was mounted on the same support and was used to drive (rotate) the external magnetic collar of the thermoregulator through a friction-belt connection. A simple spring and screw arrangement was provided to regulate the tension in the belt. A fixed rate of collar rotation was obtained in this way. As a result, the contact position of the slide wire within the mercury column which, in turn, governs the control temperature set on the thermoregulator, was varied at a constant rate. The thermoregulator was connected to a standard relay unit³ and controlled the power input to heating elements in a bath surrounding the reaction vessel.

In the majority of studies, the thermoregulator was used to control the temperatures of 1-2 L. of reactants contained in a three-neck glass flask fitted with a mechanical agitator. The mercury bulb of the regulator was placed directly into the reaction vessel which was held in an agitated water bath with approximately 5-gal. capacity. A single 500-w. immersion heater operated through the thermoregulator was used in the bath.

The time-temperature programs could be varied using synchronous motors with differing rates of rotation. It was more convenient, however, to change the rate of heating by adjusting the belt ratio between the motor and the thermoregulator collar. This was accomplished by fitting different sized sleeves onto the collar.

Constant rates of cooling also could be obtained using the control apparatus. This was achieved by inverting the position of the motor (thereby

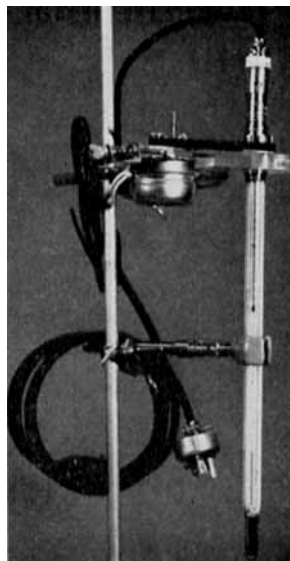


Fig. 1.—Programmed thermoregulator.

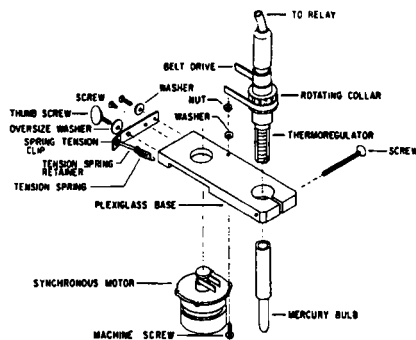


Fig. 2.—Assembly drawing of programmed thermoregulator.

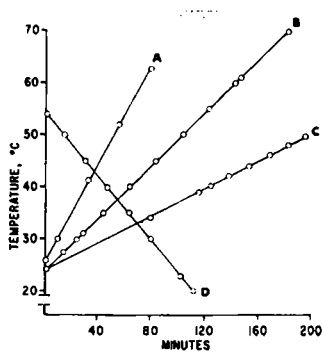


Fig. 3. — Rates of heating and cooling obtained with programmed thermoregulator.

A, 0.46° per minute; B, 0.25° per minute; C, 0.13° per minute; D, 0.30° per minute (cooling).

Received October 10, 1963, from the Department of Pharmaceutical Technology and the Instrument Shop, Warner-Lambert Research Institute, Morris Plains, N. J. Accepted for publication January 2, 1964.

* Present address: Division of Research, Development and Quality Control, Maradel Products, Inc., New York, N. Y.

¹ Thermoregulator, adjustable micro-set type, Catalog No. 62537, -10 to 110°, Precision Scientific Co., Chicago, Ill.

² Synchron motor No. 630, 1 r.p.m., Synchron Co., Homer City, Pa.

³ Electronic relay, self-contained control unit, Catalog No. 62690, Precision Scientific Co., Chicago, Ill.

reversing its direction of rotation) and by adding a cooling cell to the water bath to oppose the action of the heating element. Several typical plots of time *versus* the temperature of the reaction system obtained under these operating conditions are illustrated in Fig. 3. The constancy of the rates of heating and cooling is evident.

The programmed thermoregulator appears to have usefulness in a variety of applications where accurate control of rates of heating or cooling are required. The performance of the apparatus compares favorably with that specified for the more costly program devices which are available commercially.

Hydrogenation of 1-Naphthol with Rhodium Catalyst

By MORRIS FREIFELDER and GEORGE R. STONE

The low-pressure hydrogenation of 1-naphthol with rhodium is found to cause perhydrogenation. Use of this is made to produce *cis,cis* 1-decalol.

IN THE COURSE of studying the effect of rhodium catalysts in the hydrogenation of organic compounds, we investigated the reduction of 1-naphthol (I) under low-pressure conditions. Hydrogenation was interrupted after 2 *M* equivalents were absorbed and the resultant reaction mixture subjected to vapor-phase chromatography. A major peak consisting of about 70% of the total was identified as 5,6,7,8-tetrahydro-1-naphthol (II). In addition to a small amount of decalin and a few per cent of what appeared to be 1-tetralone, about 20% of another product was seen in the chromatograph. From its position it was suspected to be a decalol.

In view of this tendency toward overhydrogenation, it seemed worthwhile to study the reaction further. The mild conditions employed should lead to a predominance of *cis* products. It was hoped that *cis,cis* 1-decalol (III) would be obtained. If so, a less time consuming and more direct method than those described in the literature would be available.

Gutsche and Peter have prepared III in a three-step synthesis (1). Their material was of excellent quality judging from its melting point, but the conversion of II to III with freshly prepared platinum oxide required 4 days. Zimmerman and Mais, starting with I, also found that a long reduction period was necessary (2). The same slow uptake of hydrogen was encountered in another reduction in which decalin and mixed decalols were obtained as well as III (3). With Raney nickel at elevated temperature and pressure, mixtures were obtained (4).

Hydrogenation of I with rhodium catalyst at 60° and 3 Atm. did lead to III. Vapor-phase chromatography showed about 5% of decalin and almost 10% of a product which we assumed to be the intermediate 1-decalone, and a major peak (84.5%). On recrystallization of the residue from this reduction III was obtained. After several reductions at low pressure, it appeared more desirable to run the reaction at high pressure and at room temperature to convert the intermediate 1-decalone completely (if indeed it was present) and to cut down on hydrogenolysis. When the hydrogenation was carried out at 130 Atm., presumably the only product obtained

was III. On chromatography, a small amount of impurity (*ca.* 3%) was found. Infrared examination showed the absence of OH and aromatic ring and the presence of a carbonyl peak at 5.78 μ . In the absence of any conjugation, the impurity was assumed to be 1-decalone.

EXPERIMENTAL

5,6,7,8-Tetrahydro-1-naphthol.—A solution of 14.4 Gm. (0.1 mole) of 1-naphthol in 50 ml. of analytical reagent methyl alcohol was hydrogenated under 3 Atm. pressure in the presence of 4.3 Gm. of 5% rhodium on alumina catalyst.¹ Uptake of 2 *M* equivalents was complete in 5 hours. The reaction was interrupted and the solution filtered from the catalyst. After concentration, the residue solidified on cooling. Vapor-phase chromatography² showed 0.72% decalin, 20.4% of decalol or decalols, 69% of a tetrahydronaphthol, plus about 7% of two unknowns. The mixture on infrared examination³ showed presence of OH, aromatic ring, and a carbonyl peak at 5.9+ μ (1-tetralone shows a peak at 5.98 μ).

The mixture was then dissolved in benzene and extracted with 100 ml. of 50% sodium hydroxide solution. The alkaline solution was acidified and extracted with benzene. The benzene extract was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was treated with hexane and allowed to stand to crystallize. The product obtained melted at 68° (described 68.5 to 69°) (1) and was shown to be 5,6,7,8-tetrahydro-1-naphthol by mixed melting point and infrared absorption compared to a known standard.

***cis,cis* 1-Decalol.**—The hydrogenation of 0.1 mole of 1-naphthol was carried out at 60° and 3 Atm. in the presence of 5.8 Gm. of 5% rhodium on carbon.¹ Uptake for 5 H₂ was complete in 12 hours. After removal of catalyst and solvent, the residue obtained solidified and melted at 77–86° with softening at 70°. Recrystallization from heptane raised the melting point to 90 to 91.5° (described 93°) (1). The crude material was examined by means of vapor-phase chromatography. Results showed 5.4% decalin, 9.6% of an unidentified fraction (possibly 1-decalone), and 84.3% of III.

A second set of runs was carried out as above. The residue was distilled. Decalin was again obtained, the remainder of the material distilled over a wide range, 210–237° at atmospheric pressure.

Received November 18, 1963, from the Organic Chemistry Department, Research Division, Abbott Laboratories, North Chicago, Ill.

Accepted for publication January 2, 1964.

¹ Available from Engelhard Industries, Newark, N. J.

² Carried out by P. F. Helgren of this laboratory.

³ Carried out by W. Washburn and A. Kammer of this laboratory.