

Cape Cleare was detailed in 1927. This area may prove to be one of extensive uplift if analyzed by comparative surveys of the type used in this study.

RICHARD J. MALLOY

U.S. Coast and Geodetic Survey,  
Washington, D.C. 20230

#### References

1. U.S. Department of Commerce, Coast and Geodetic Survey, hydrographic smooth sheet H 4730 (1927).
  2. U.S. Department of Interior, Geological Survey, press release dated 23 July 1964.
- 26 October 1964

### Coupling of Butyl Bromide on Hot Magnesium

**Abstract.** *A report of the formation of octane when butyl bromide is passed over magnesium turnings at high temperatures should be amended. Such coupling does take place over pure magnesium at more moderate temperatures but yields 3-methylheptane and sec-butyl bromide in addition to octane. Sec-butyl bromide itself forms no coupling product under such conditions but admixed with butyl bromide markedly increases the 3-methylheptane:octane ratio in the product.*

A previous note in *Science* (1) stated that butyl bromide, when passed with helium through a tube containing magnesium turnings at 330°C, formed 10 percent of octane. Using magnesium turnings of high purity (2) we were unable to reproduce these findings, despite many attempts with varying tube lengths, tube geometry, contact times, and temperatures between 275° and 400°C (3). The effluent, condensed in ice and dry-ice traps and then freed of HBr by washing with sodium hydroxide solution, was analyzed by gas chromatography (4) after being dried.

Very small quantities of coupling products were obtained in only one experiment of the many carried out in the range of 300°C. In contrast, when the butyl bromide was passed over pure magnesium at 150° to 200°C, coupling could be effected routinely after a variable induction period. Yields depended on the rate of addition of the butyl bromide and careful maintenance of the experimental conditions.

Analysis of the product by gas chromatography showed the presence of 2.6 percent (of the theoretical

yield) of octane (5), 4.4 percent of 3-methylheptane (5), and 3.6 percent of sec-butyl bromide resulting from a typical experiment when 0.8 ml of butyl bromide per minute was dropped on the magnesium turnings at 150° to 200°C in the presence of 30 ml of helium per minute. Lower boiling products were not investigated; butanes and butenes were present in significant quantities. At an addition rate of 0.02 ml of butyl bromide per minute, yields of 4.6 percent of octane, 11.6 percent of 3-methylheptane, and 2.5 percent of sec-butyl bromide were more typical.

When pure sec-butyl bromide was the feed substance, no coupling on magnesium at 150° to 200°C was detected, even though the analytical method would have shown even a few tenths of a percent of octane, 3-methylheptane, or the possible coupling product, 3,4-dimethylhexane. However, when a mixture of two volumes of butyl bromide to one of sec-butyl bromide was used under the usual conditions with a drop rate of 0.02 ml per minute, 1.0 percent of octane and 8.0 percent of 3-methylheptane were produced.

Although the present investigation has not established the radical or ionic character of the reaction on hot magnesium, any satisfactory mechanism must account for the several findings: the rearrangement of butyl bromide to sec-butyl bromide under our reaction conditions, the nonoccurrence of the reverse process, the production of 3-methylheptane from butyl bromide plus the reactive intermediate derived from sec-butyl bromide, and the lack of formation of 3,4-dimethylhexane from sec-butyl bromide.

FRANK L. LAMBERT, WILLIAM D. ELLIS

NELSON F. PHELAN, CARL F. FLEGAL  
Department of Chemistry,  
Occidental College, Los Angeles

#### References and Notes

1. A. Turk, M. P. Zimmerman, R. Mavis, *Science* **110**, 332 (1949).
2. Sublimed magnesium was provided through the courtesy of J. F. Pashak of the Wrought Development Section of the Dow Metal Products Company.
3. This negative finding is not disparaging to the results of Turk and co-workers; it points up the complexities of the reaction. Small quantities of metal impurities in the magnesium influence the course of the reaction, and temperatures in the reaction tube may vary widely unless unusually careful control is exerted.
4. A Research Specialties gas chromatograph fitted with a 2-m Apiezon L column (about 10 percent on 60-80 mesh Chromosorb P) and a katharometer detector were used for analytical runs. Quantitative results were verified by calibration with known mixtures.
5. Identity was conclusively established by infrared analysis (Perkin-Elmer 237 spectrophotom-

eter) of macroquantities which were isolated from the product mixture by an Autoprep gas chromatograph (Wilkins Instrument and Research, Inc.) fitted with a 6 m × 0.9 cm column filled with 20 percent SE-30 on 60-80 mesh Chromosorb W.

6. This work was initiated by a Research Corporation grant. The authors thank D. F. Clark for preliminary studies and designs of equipment. W.D.E., N.F.P., and C.F.F. were aided in their work by the National Science Foundation undergraduate science education program under grants GE-2797, GE-987, and GE-12126.

14 September 1964

### Rubidium-Strontium Isochron Study of the Grenville Front near Lake Timagami, Ontario

**Abstract.** *Rubidium-strontium isotopic analyses of whole-rock samples and of constituent minerals from a suite of rocks taken across the Grenville Front demonstrate that granitic rocks of the Superior province, with a primary age of approximately 2.4 billion years, and older metasedimentary rocks were reconstituted during Grenville metamorphism, at approximately 930 million years, and now form part of the Grenville province.*

In understanding the evolution of continental masses, the question of the growth of continental bodies through geologic time is of fundamental importance. Parts of the North American continent have been subdivided on the basis of geologic characteristics and apparent age. With regard to the hypothesis of continental accretion it is necessary to determine whether the geologically younger parts of the continental masses represent the addition of new material or are in fact the product of metamorphism of the older pre-existing geologic provinces. The boundaries between old and young provinces are the natural places to study these possible phenomena. Reported herein are some of the characteristics of a portion of the boundary zone between the Grenville and Superior provinces as shown by a study of strontium and rubidium isotopes.

The Grenville Front is the northwestern boundary of the Grenville province of the Canadian Shield (see Fig. 1). For over 800 miles it forms the boundary between the Superior and Grenville provinces (1, 2). These provinces differ in particular in structure and in grade and age of major metamorphism. The easterly trending structures of the Superior province are truncated on the southeast by the northeasterly trending structures of the Grenville.