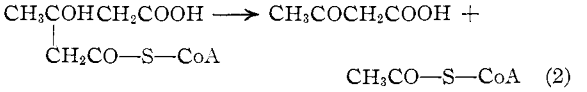
Since the product is a mono CoA ester of HMG, the problem arises whether the thioester bond of Ac CoA or of AcAc CoA is hydrolyzed during the condensation reaction. This problem was resolved in the following manner: HMG CoA enzymatically formed by the condensing enzyme from acetyl-1-C^{14} CoA and AcAcCoA was mixed with carrier HMG CoA[9] and cleaved by the HMG CoA cleavage enzyme of Bachhawat, *et al.*,[10] to acetoacetic acid and AcCoA according to reaction 2.



$$\underset{\displaystyle \mathrm{CH_2CO—S—CoA}}{\mathrm{CH_3COHCH_2COOH}} \longrightarrow \mathrm{CH_3COCH_2COOH} + \mathrm{CH_3CO—S—CoA} \quad (2)$$

Decarboxylation of the acetoacetic acid to acetone and CO_2 showed the radioactivity to reside solely in the CO_2. These results show that the free carboxyl group of HMGCoA contained C^{14}. Since the C^{14} was originally in the carboxyl position of acetyl-1-C^{14} CoA it may be concluded that the CoA set free during the condensation reaction came from AcCoA according to reaction 1.[11]

Since HMG CoA is the product of the condensation reaction, we would redesignate the enzyme as the HMG CoA condensing enzyme. This enzyme resembles the citrate condensing enzyme,[12] in that (1) Ac CoA condenses with the carbonyl group of the other substrate, and (2) a net hydrolysis of Ac CoA results. The enzyme appears to be specific for thioesters of CoA, since the corresponding thioesters of pantetheine and glutathione were inactive. Efforts to reverse the condensation have been unsuccessful thus far.

At the present time two ways are known in which HMG CoA can be formed, the first *via* the condensation reaction described above, and the other the CO_2 fixation reaction of Bachhawat *et al.*[13] The obvious relationship between HMG CoA and mevalonic acid, a compound efficiently converted to cholesterol,[14] is under investigation.

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[9] Prepared from HMG anhydride by the method of E. J. Simon and D. Shemin, THIS JOURNAL, **75**, 2520 (1953).

[10] B. K. Bachhawat, W. G. Robinson and M. J. Coon, *J. Biol. Chem.*, **219**, 539 (1956). We are grateful to Dr. M. J. Coon for a sample of the HMG CoA cleavage enzyme.

[11] This result would also be obtained if an intramolecular transfer of CoA occurred from one carboxyl group of HMG CoA to the other. This possibility appears to be eliminated by experiments (H. Rudney and T. G. Farkas, *Federation Proc.*, **14**, 757 (1955); M. J. Coon, *J. Biol. Chem.*, **187**, 71 (1950); G. W. E. Plaut and H. A. Lardy, *ibid.*, **186**, 705 (1950)) which demonstrated that when $C^{14}O_2$ was fixed into acetoacetate by liver homogenates, assuredly *via* HMG CoA formation and subsequent cleavage to acetoacetate and Ac CoA, isotope appeared almost exclusively in the carboxyl group of acetoacetate. If intramolecular CoA transfer occurred between the carboxyls of HMG CoA, then after cleavage the thiolase present in the homogenates would have randomized the label between the carboxyl and carbonyl carbons of acetoacetate.

[12] J. R. Stern, S. Ochoa and F. Lynen, *J. Biol. Chem.*, **198**, 313 (1952).

[13] B. K. Bachhawat, W. G. Robinson and M. J. Coon, *ibid.*, **216**, 727 (1955).

[14] P. A. Tavormina, H. M. Gibbs and J. W. Huff, THIS JOURNAL, **78**, 4498 (1956).

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THE SCAVENGER EFFECT IN SOLID ETHYL BROMIDE

Sir:

During an investigation of the Szilard–Chalmers effect in solid ethyl bromide, it was found possible to produce a solid phase containing variable proportions of elementary bromine. This technique could prove useful in the study of the rather complicated reactions following (n,γ) processes in solid organic halides.[1]

The ethyl bromide and bromine used were purified as described elsewhere[2] and mixtures of these were frozen using liquid nitrogen. Twenty-five cc. of the mixture was contained in a narrow necked glass vessel into which a quartz tube was fitted. Two methods of freezing were used. In the first, liquid nitrogen was poured into the central quartz tube and complete freezing occurred in about one hour; using the second method, the freezing time was reduced to 5 minutes by also immersing the vessel in liquid nitrogen. In the latter case, care was taken to transform any transparent glass produced on the walls of the vessel into opaque crystals[1a] by leaving it at room temperature for a minute before irradiation. The sealed vessel containing the frozen mixture was placed in a Dewar fitting in a paraffin moderator castle. A 500 mc. polonium–beryllium source was lowered into the center of the quartz tube which was kept full of liquid nitrogen during irradiation (50 minutes). After irradiation, the solid was left to melt at room temperature and the liquid was extracted with an aqueous sodium sulfite solution. The activities due to Br^{80} (18 min. half-life) in the unextracted and extracted specimen were determined, the activity of the other bromine isotopes being negligible.[3]

The results obtained are shown in Fig. 1 curve (a), where the retention[4] has been plotted against the molar fraction of the elementary bromine present. The speed of freezing did not influence the retention of pure ethyl bromide. When bromine was present, an appreciable drop in retention was only observed when the faster freezing method was used (see Table I).

TABLE I

Mol. fract. of Br	Freezing time	Retention of Br^{80}, %
0	1 hour	$83.0 + 2.6$
0	5 min.	$82.1 + 2.6$
0	5 min.	$82.0 + 2.5^a$
$5,7.10^{-2}$	1 hour	$78.2 + 2.3$
$5,7.10^{-2}$	5 min.	$69.5 + 2.2$

[a] This specimen was allowed to melt in the presence of 3.8 cc. of a solution of bromine (0.38 molar fraction) in ethyl bromide.

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[1] (a) F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1495 (1953); (b) L. Friedman and W. F. Libby, *ibid.*, **17**, 647 (1949); (c) S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951); (d) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

[2] Miriam Milman and P. F. D. Shaw, *J. Chem. Soc.*, 1303 (1957).

[3] Details of precautions taken, counting technique and corrections applied have been previously reported.[2]

[4] The retention is defined as the fraction of the total activity present in organic combinations.

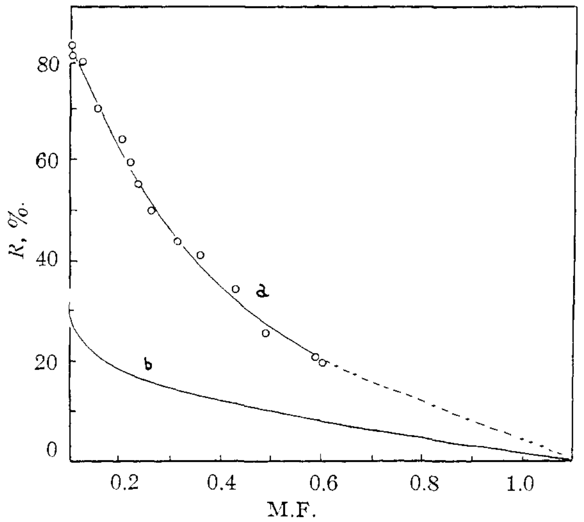

Fig. 1.—Retention of solid ethyl bromide (curve "a") and liquid ethyl bromide (curve "b") as a function of the molar fraction of bromine.

The purpose of experiment (a) was to determine whether free organic radicals were trapped in the solid. The constancy of the retention indicates either that such radicals do not exist or, that they react before mixing with the scavenger solution. The reproducibility of the results obtained using the second method of freezing bromine–ethyl bromide mixtures was checked by repeating a number of experiments at the same bromine concentration. No variations beyond statistical limits were observed, even though the freezing time varied from 3 to 5 minutes.

These preliminary results show that the drop in retention caused by the addition of small quantities of bromine is less sharp than that observed in liquid ethyl bromide (Fig. 1b). To clarify the nature of the processes involved we are now carrying out experiments to identify the radioactive products obtained and to determine the comparative behavior of the bromine isotopes produced by (n, γ) processes.

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RHOMBOHEDRAL ELEMENTAL BORON

Sir:

The simultaneous occurrence of two widely dissimilar external forms for single crystals of pure boron growing[1] on a hot filament was thought[1,2] for a time to reflect true structural polymorphism, but comprehensive diffraction studies[3] show that, at least in the work cited,[1] a single structural type is represented: namely, the atomic arrangement based upon a fifty-atom *tetragonal* unit earlier described.[2] That there exists, nevertheless, a second, and probably more commonly obtained modification of boron has seemed certain from published powder diffraction data. For example, the interplanar spacings listed[4] for prominent powder lines given by a sample of better than 99% purity (unspecified method of preparation) are wholly incompatible with our tetragonal cell. Recently we have obtained from independent sources two preparations of boron briefly characterized as follows: the stated purities are 99.4 and 99.5% B but the preparative chemical methods are withheld; both are aggregates of small single crystals resulting from crystallization of the melt, and both afford specimens suitable for single crystal study; and they give a common powder diagram which includes the lines listed by Godfrey and Warren.[4] Dr. S. Geller of the Bell Telephone Laboratories provided us with Preparation I. Amorphous boron, supplied by Cooper Metallurgical Associates, was melted partially in a "Heliarc" furnace and allowed to crystallize in a helium atmosphere by E. Corenzwit of the Bell Laboratories. Preparation II, received within the fortnight, came to us from the United States Borax & Chemical Corporation through the good offices of Professor A. W. Laubengayer.

Oscillation, Weissenberg, and precession photographs of single crystals from Preparation I establish a *rhombohedral* lattice having $a = 10.12$ Å, α 65°28′; the associated triply primitive hexagonal cell has $A = 10.95$, $C = 23.73$ Å, accurate to 0.2%. The experimental density, 2.35 ± 0.01 g./cc., is equally consistent with 107 or 108 atoms within the rhombohedral unit. The diffraction symmetry and lack of glide plane vanishings indicate R$\bar{3}$m, R32, or R3m as the space group. Spectrometrically measured intensity data (using both Cu Kα and Mo Kα radiations) have been obtained for two zones, *i.e.*, with the hexagonal A and rhombohedral a as zone axes. The statistical distribution of intensities is centrosymmetric[5] for the first zone, hypercentric[6] for the second, thus supporting the unique choice of R$\bar{3}$m as the space group. We note that boron carbide[7] also crystallizes in R$\bar{3}$m, with $a = 5.19$ Å, $\alpha = 65°18'$ so that all lattice translations are approximately half the corresponding values in rhombohedral boron. However, there is no suggestion in the boron data of a pseudo-unit comparable in volume or obviously related in structure to the boron carbide unit. Although undoubtedly belonging to a more complex structural type, our rhombohedral boron affords intensity data showing little or no evidence for the presence of the large and variable concentrations of short-range defects which seem to characterize[3] all actual specimens of tetragonal boron as grown

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(1) A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

(2) J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).

(3) J. L. Hoard, R. E. Hughes and D. E. Sands, to be submitted to THIS JOURNAL.

(4) T. N. Godfrey and B. E. Warren, *J. Chem. Phys.*, **18**, 1121 (1950).

(5) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(6) H. Lipson and M. M. Woolfson, *ibid.*, **5**, 680 (1952).

(7) H. K. Clark and J. L. Hoard, THIS JOURNAL, **65**, 2115 (1943); G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U.R.S.S.*, **32**, 432 (1941).