of fission recoil fragments. The thermal neutron dose during irradiation was monitored using high purity cobalt wire, and energy deposition (extending to 5 × 10^{21} e.v. per g. of solution) was calculated assuming 160 Mev. of recoil energy released per fission event,[2] and a thermal neutron fission cross-section for U^{235} of 580 barns.[3] The main products were hydrogen, oxygen and nitrogen, with smaller amounts of carbon dioxide, and, in the case of concentrated nitrate solutions, nitrous oxide. With more dilute solutions, precipitation of some UO_4 during irradiation was encountered. As this phenomenon would have introduced uncertainty into energy deposition data, it was prevented by adding about 100 p.p.m. of iron as ferric nitrate to the solutions; this presumably catalyzed the deposition of H_2O_2 sufficiently to prevent peroxide precipitation. No peroxide and only traces of nitrite were found in solution after irradiation.

A plot of G_{H_2} *vs.* $(NO_3^-)^{1/3}$ is linear, and obeys an equation of the type $G_{H_2} = A - k(NO_3^-)^{1/3}$, (1) where $A = 2.0$ and $k = 0.8$: the G_{H_2} data of Boyle and Mahlman for $Th(NO_3)_4$-$U^{235}O_2(NO_3)_2$ solutions also lie on this line. The results can therefore be explained qualitatively in terms of a theory[1] involving reaction of diffusing H atoms with NO_3^-: $NO_3^- + H \rightarrow NO_2 + OH^-$ (2), where the parameter k is a measure of the probability of reaction (2).

Values of G_{N_2} are more than an order of magnitude greater than those obtained for fast neutron-γ energy. Figure 1 shows a log–log plot of G_{N_2} *vs.* (NO_3^-), and includes the present data, those of Boyle and Mahlman,[4] and those of Bidwell, *et al.*,[6] obtained from experiments with critical assemblies of uranyl nitrate solutions (the Los Alamos "water boilers"). The continuity of the curve indicates that cation variation has little effect on nitrogen yields. The present data were obtained at about 80°, while the American data correspond to temperatures ranging from 37° to 300°; temperature has therefore no significant effect on G_{N_2}.

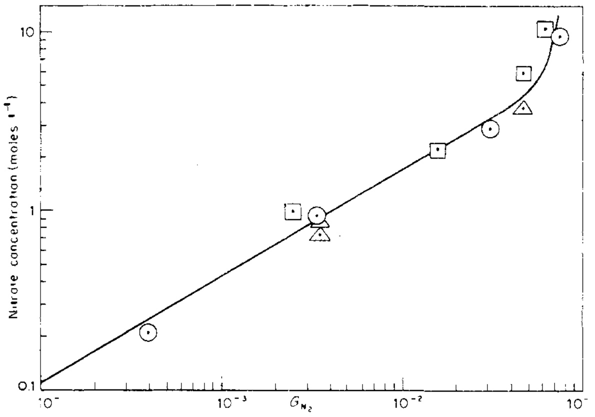

Fig. 1.—Log–log plot of G_{N_2} vs. $[NO_3^-]$: ○, present results; □, data of Boyle and Mahlman; △, data of Bidwell.

Below a nitrate concentration of about 4*M*, nitrogen yields can be expressed by the empirical relationship $G_{N_2} = 0.004(NO_3^-)^{1.5}$ (3), though nothing can be said at this stage about the mechanism of nitrogen formation.

A complete account of the work, with due acknowledgments, will be published elsewhere.

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(2) S. Glasstone, "Source Book on Atomic Energy," Macmillan, 1950.

(3) Brookhaven National Laboratory, "Neutron Cross Sections," B.N.L.-235, Supplement 1 (1957).

(4) J. W. Boyle and H. A. Mahlman, *Nucl. Sci. Eng.*, **2**, 492 (1957).

(5) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

(6) R. M. Bidwell, L. D. P. King and W. R. Wykoff, *Nucl. Sci. Eng.*, **1**, 452 (1956).

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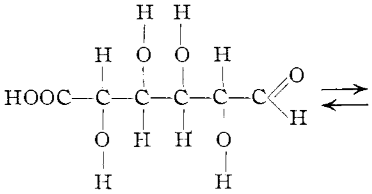
ENZYMATIC FORMATION OF D-TAGATURONIC AND D-FRUCTURONIC ACID

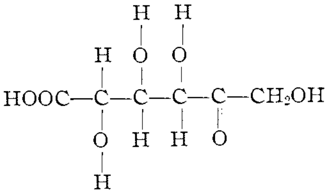
Sir:

Various microörganisms have been shown to metabolize uronic acids rapidly although little is known about the nature of the primary reaction products formed.[2,3,4] In the present study, D-tagaturonic acid (II) and D-fructuronic acid (IV) have been identified as the first products in a new pathway for the metabolism of D-galacturonic acid (I) and D-glucuronic acid (III), respectively.



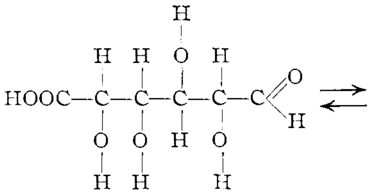
$$HOOC{-}\underset{OH}{\overset{H}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}C{\overset{O}{\underset{H}{\lessdot}}} \rightleftarrows$$

I



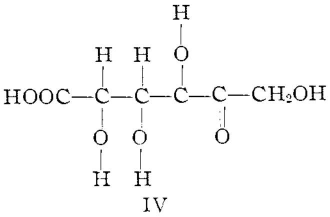
$$HOOC{-}\underset{OH}{\overset{H}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{O}{\overset{}{C}}{-}CH_2OH$$

II



$$HOOC{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}C{\overset{O}{\underset{H}{\lessdot}}} \rightleftarrows$$

III



$$HOOC{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\overset{OH}{C}{-}\underset{O}{C}{-}CH_2OH$$

IV

Cultures of *E. coli* (ATCC 9637) were grown aero-

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(1) D-Tagaturonic acid may also be designated as 5-keto-D-altronic acid, 5-keto-L-galactonic acid or, systematically, D-*arabino*-5-hexulosonic acid. Similarly, D-fructuronic acid may be designated as 5-keto-D-mannonic acid, 5-keto-L-gulonic acid or D-*lyxo*-5-hexulosonic acid.

(2) S. S. Cohen, *J. Biol. Chem.*, **177**, 607 (1949).

(3) P. J. Heald, *Biochem. J.*, **50**, 503 (1952).

(4) M. P. Starr, J. DeLey and W. W. Kilgore, *Science*, **125**, 929 (1957).

bically on a minimal salt medium containing D-galacturonic acid as the sole carbon source. After 24 hours at 37°, the cells were harvested, disrupted by sonic vibration and the extract partially purified by isoelectric precipitation.

A reaction mixture containing 50 μmoles of either I or III was incubated separately with the extract for one hour at 37° and the reaction products isolated by chromatography on Dowex-1-formate[5] or by paper chromatography with ethyl acetate: acetic acid:water (3:1:3) as the solvent system. In either case, there was a clear separation of unreacted starting material and of a more rapidly moving component which was isolated and identified as II or IV, respectively.

Both of the unknown products gave color reactions characteristic of uronic acids[6,7] but which were stable to bromine water under conditions where the alduronic acids were completely oxidized. Upon treatment with HIO_4 under acidic conditions,[8] formaldehyde was not formed and the presence of a 2-keto acid therefore presumed unlikely. Quantitative measurement at pH 6.2[9] showed that 3.1 and 2.6 moles of HIO_4 were taken up per mole of II and IV, respectively. The glycolic acid formed[10] was 1.0 and 1.1 moles per mole of II and IV, a result in close accord with the theoretical values for 5-keto acids.

Further evidence that the enzymatic reaction products were II and IV was provided by reduction with KBH_4. The resulting aldonic acids were lactonized and chromatographed on paper in three different solvent systems. Upon visualization of the lactones with hydroxylamine and $FeCl_3$,[11] it was seen that II yielded galactono- and altronolactones while IV yielded gulono- and mannonolactones. These results are definitive for the structures as written.

The crystalline brucine salt of D-fructuronic acid was prepared by a modification of the procedure used to synthesize crystalline D-tagaturonic acid.[12] Paper chromatography in several solvents revealed that II invariably co-chromatographed with authentic D-tagaturonic acid and that IV acted similarly with pure D-fructuronic acid. Upon incubation of the synthetic keturonic acids with the enzyme, the formation of the corresponding alduronic acids (I or III) was readily demonstrable. Finally, the crystalline brucine derivatives of II and IV were prepared and checked by mixed melting points with the authentic derivatives.

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RECEIVED MARCH 24, 1958

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(5) J. X. Khym and D. G. Doherty, THIS JOURNAL, **74**, 3199 (1952).

(6) Z. Dische, *J. Biol. Chem.*, **167**, 189 (1947).

(7) W. Z. Mejbaum, *Z. physiol. Chem.*, **258**, 117 (1939).

(8) J. MacGee and M. Douderoff, *J. Biol. Chem.*, **210**, 617 (1954).

(9) B. L. Horecker, J. Hurwitz and A. Weissbach, *J. Biol. Chem.*, **218**, 785 (1956).

(10) S. Dagley and A. Rodgers, *Biochim. et Biophys. Acta*, **12**, 591 (1953).

(11) M. Abdel-Aker and F. Smith, THIS JOURNAL, **73**, 5859 (1951).

(12) F. Ehrlich and R. Guttman, *Ber.*, **67**, 1345 (1934).

(13) Fellow of the Damon Runyon Memorial Fund for Cancer Research.

INHIBITION OF CRYSTALLIZATION IN POLYETHYLENE SUBSEQUENT TO GAMMA IRRADIATION

Sir:

Recent results[1] suggest that irradiation of polyethylene at room temperature and doses below 29 × 10^{20} e.v.g.$^{-1}$ causes no change[2] in crystallinity, but that on fusion and solidification subsequent to the irradiation, the crystallinity decreased.[2] We have confirmed these results by a direct measurement at room temperature of the amorphous content of polyethylene utilizing the infrared absorption bands[3] at 1080 and 1303 cm.$^{-1}$.

The open circles of Fig. 1 demonstrate the constancy of the crystallinity of 85% crystalline Marlex-50 during irradiation at room temperature with Co-60 γ-rays while the vertical arrows indicate the growth of relative amorphous content, ϕ_A, on post-irradiation fusion and solidification. The four solid circles represent data obtained at room temperature subsequent to irradiation at 140°. The post-irradiation fusion also causes additional vinyl decay and vinylene growth.[4]

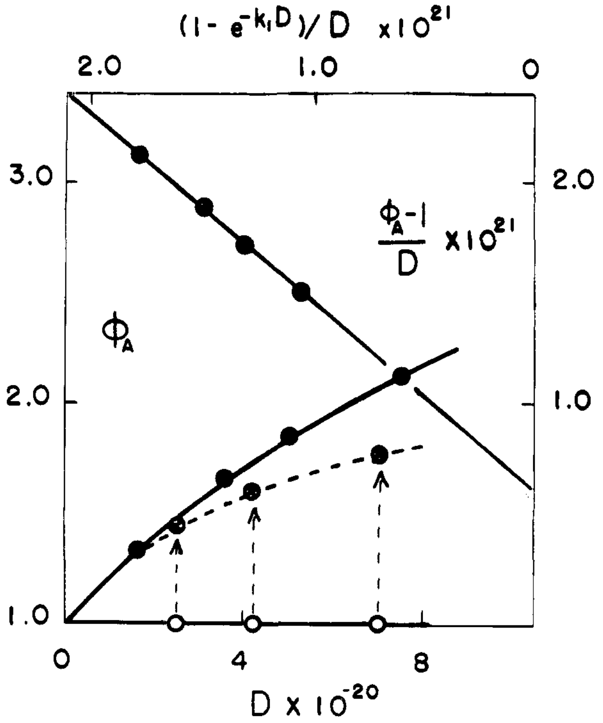

Fig. 1.—Open circles, are relative amorphous content (ϕ_A) of Marlex-50 polyethylene as a function of room temperature irradiation; solid circles, ϕ_A for irradiation at 140°. The dotted lines indicate the growth in amorphous content during post-irradiation fusion and solidification. Upper straight line is a test of Eq. (2).

Hitherto, only the effect of cross linking on crystallinity has been considered, but the following

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(1) A. E. Woodward, C. W. Deeley, D. E. Kline and J. A. Sauer, *J. Polymer Sci.*, **26**, 383 (1957).

(2) M. Dole and W. H. Howard, *J. Phys. Chem.*, **61**, 137 (1957).

(3) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).

(4) M. Dole, T. F. Williams and A. J. Arvia, paper submitted to the 2nd International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958.