A specific activity of 87 mC./g. was obtained by subjecting polyethylene glycol to 28.7 watt h. of microwave energy but the material may not have been sufficiently purified. A sample (180 mg.) of blood serum albumin was treated with the microwave technique in the presence of 51 mc. of tritium for 90 sec. at 110 watt microwave power. The sample was purified by dialysis, separated by paper electrophoresis and measured in a Tri-carb liquid scintillation counter. The steady specific activity was 5 μC./mg.[3] Due to the very short reaction time, the method can be recommended—especially when using a bent tube, a technique which has not yet been explored—for the internal labelling of radiation sensitive materials such as proteins.

Runs were performed using benzene. In a typical run, 88 mg. of frozen benzene and 76 mC. of tritium were treated for 2 min. at 40 watt microwave power. After the discharge, a thin film of polymeric material was observed. The degree of labelling of benzene was tested by measuring the specific activity of *m*-dinitrobenzene after isotopic dilution with ordinary benzene, dinitration[4] and repeated crystallizations from ethyl alcohol to constant radioactivity. The specific radioactivity of *m*-dinitrobenzene was 3 mC./g. which corresponded to a specific activity of benzene in the original sample of 218 mC./g. assuming no decomposition. This was further confirmed by mass spectrometry of the samples.

A special case of "specific labelling" arose when the energy-rich ethylene oxide was treated by the above technique at a suggestion by Dr. L. Ehrenberg. The treated material was isotopically diluted and fractionally distilled. It was preliminarily found[5] that almost all the radioactivity went to the ethyl alcohol formed from the ethylene oxide and very little to the ethylene oxide. The specific activity of the alcohol is high according to the measurements.

Tubes with stainless steel and aluminum electrodes were constructed in order to study labelling processes with glow discharges. 30–60 mg. of powdered polystyrene was used in each run. In all experiments, a glow discharge of 1–5 w. either d.c. or 50 hz. a.c. was produced and the tritium pressure went rapidly down to 5% of the original pressure. Specific activities ranging from 5–31 mC./g. were obtained. The percentage of total tritium fixed ranged from 1.6–16 with a fixation yield of 0.006–0.012 mC./watt sec. Bremsstrahlung measurements showed less than 1 mC. in the steel electrodes for both the a.c. and the d.c. experiments.

Experiments also were performed under such conditions that a reaction of tritium atoms was just possible energetically. A low pressure ultraviolet lamp was used, emitting predominantly 2537 Å. corresponding to 4.88 eV. of quantum energy. The energy required to dissociate a hydrogen molecule into atoms is 4.476 eV.[5] The bond energy of T_2 can be estimated by the method of ref. (6) to be greater than that of H_2 by 0.11 eV. (using the vibration energy difference given in ref. (7)) and therefore the energy required to atomize tritium may be taken as 4.59 eV. which is somewhat lower than the energy supplied by the 2537 Å. quanta. It might be recalled that it is known that the 2537 Å. line atomizes H_2 by mercury photosensitizing.[8] Polystyrene (300 mg.) which absorbs in the ultraviolet and polymethyl methacrylate (300 mg.) which almost does not absorb at all were irradiated separately in evacuated quartz tubes by a "Mineralight" lamp (50 watts) for 24 hr., each in the presence of 100 mC. of tritium. Labelled polystyrene of 20 mC./g. and labelled polymethyl methacrylate of 31.1 mC./g. were produced. The smell of monomeric methyl methacrylate and the high activity (12 mC.) in the purifying liquids indicated a chain-end degradation of the polymer. These results substantiate the atomic mechanism for the reaction of tritium with organic materials under these accelerating conditions. We might tentatively assume that the polymeric substances in these cases act as sensitizers for the atomization process. (Mercury was not present.)

The above findings extend the field for the production of labelled material because of the rather simple techniques, limited decomposition and considerable saving of time, material and safety precautions. We feel that even more favorable conditions might be found along these lines.[9]

N. A. G. is grateful to The International Atomic Energy Agency for a Fellowship.

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(3) Dr. S. Ullberg, private communication.

(4) Muspratt and Hofmann, *Liebigs Ann.*, **57**, 214 (1845).

(5) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958, see p. 173.

(6) L. Melander, *Arkiv för Kemi*, Band 2, no. 12, 241 (1950).

(7) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry, Macmillan Co., New York, N. Y. 1952, p. 11.

(8) T. Rummel, "Hochspannungsentladungschemie und ihre industrielle Anwendung," München, 1951, p. 130 footnote 1, where the author quotes work by Cario and Franck.

(9) N. A. Ghanem, L. Ehrenberg and N. T. Natarajan, to be published.

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RECEIVED JUNE 8, 1960

THE PREPARATION OF INTERLOCKING RINGS: A CATENANE[1]

Sir:

This report describes the formation of a macrocyclic acyloin in the presence of a macrocyclic hydrocarbon to give a small but demonstrable yield of a catenane.[1] The existence of interlocking rings in polysiloxanes[2] and polymeric phosphonitrile chloride[3] has been suggested by some workers. An unsuccessful attempt to prepare a well-defined chemical species with such non-bonded rings has also been discussed.[4]

Diethyl tetratriacontanedioate (I) was prepared by the method of Fairweather.[5] Reaction of I

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(1) "Catenane" (Latin, *catena*, chain) is suggested as a generic name for systems such as V.

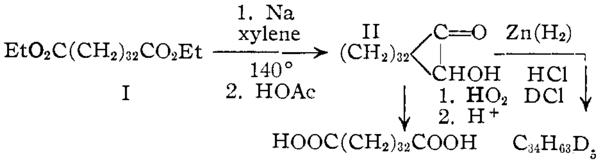
(2) H. Frisch, I. Martin and H. Mark, *Monatsh.*, **84**, 250 (1953).

(3) F. Patat and P. Derst, *Angew. Chem.*, **71**, 105 (1959).

(4) A. Lüttringhaus, F. Cramer, H. Prinzbach and F. M. Henglein, *Ann.*, **613**, 185 (1958). The interesting approach of H. Kohler and D. Dieterich, D. P. 1069617, apparently requires some additional experimental work; see *Nach. Chemie und Technik*, **8**, 87 (1960), in *Angew. Chem.*, **72**, No. 6 (1960).

(5) D. A. Fairweather, *Proc. Roy. Soc. Edinburgh*, **45**, 283 (1925). The final electrolysis followed the procedure of L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, **16**, 496 (1933).

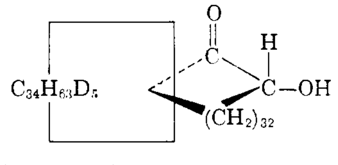
with sodium yielded the cyclic acyloin (II). *Anal.* Calcd. for $C_{34}H_{66}O_2$: C, 80.56; H, 13.12: O, 6.31. Found: C, 80.66; H, 13.00, O, 6.44. Clemmensen reduction of II with deuterated hydrochloric acid produced the cyclic hydrocarbon (III), in 50% yield from I, m.p. 67–68,°[6] with *ca.* 5 atoms of deuterium per molecule. The transformation of I to II was then carried out with a 1:1 mixture of III and xylene as solvent.



Unchanged III was separated *cleanly* from the other products by chromatography using pentane as eluent. The fraction containing II, which was removed with ether–methanol, had infrared bands at 2105, 2160 and 2200 cm.$^{-1}$ (C–D stretch) which were also observed in the spectrum of III. Rechromatography of this material demonstrated that the deuterium was associated with the acyloin and was not due to contamination by unaltered III. This acyloin fraction was oxidized with alkaline hydrogen peroxide giving the diacid (IV). The presence of III among the products was demonstrated by its chromatographic behavior, infrared spectrum, m.p. and mixed m.p. The yield of II, formed in the presence of III, varied between 5 and 20%. The yield of III in a given oxidation was roughly proportional to that of II and constituted about 1% of the acyloin.[7]

It is proposed that the acyloin fraction contains V, a species comprised of two interlocking but otherwise non-bonded rings. Oxidation of V cleaves the acyloin containing ring and this is followed by unthreading to give III. It is unlikely that some other deuterated system would give rise to III under oxidative conditions. Chromatography of the material obtained by heating III, xylene and sodium with II, previously formed in the absence of III, gave *no* deuterium in the acyloin fraction. Oxidation of that fraction produced no hydrocarbon.

V



We note that V is the first demonstrated example of a compound in which the topology of the system must be considered in describing its structure. For example, V is a topological "isomer" of the non-interlocked system II plus III.[8] Other possibilities for topological isomers exist,[9] *e.g.*, models indicate that a cycloalkane of more than 50 carbon atoms can take the form of a simple or a knotted ring. In addition, this latter species can exist in two optical isomers.

Further work with larger quantities of material to permit isolation of V is in progress.

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[6] L. Ruzicka, M. Hürbin and M. Furter, *Helv. Chim. Acta*, **17**, 78 (1934) found m.p. 66°–67° for non-deuterated III.

[7] Calculations by H. Frisch have given a probability of 10^{-2} for this statistical threading. This small value renders the hypothesis of extended chains of references 2 and 3 somewhat less likely. It also reduces the probability that more than 1% of III, from the oxidation reaction, arose from higher interlocked systems.

[8] Thus two separate molecules are to be viewed as isomeric with V, which resembles a single molecule in many respects. It should be noted that topological isomers necessarily have identical chemical bonding and arrangements of atoms about rigid centers.

[9] H. Frisch and E. Wasserman, Division of Polymer Chemistry, 138th Meeting A.C.S., New York, Sept., 1960.

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RECEIVED JULY 5, 1960

THE MECHANISM OF BASE HYDROLYSIS AND BASE CATALYZED REACTIONS OF SOME COBALT(III) AMMINE COMPLEXES

Sir:

Two mechanisms have been proposed for the reaction of hydroxide ion with complexes of cobalt (III) containing a replaceable ligand. One is the direct displacement, or SN2 mechanism[1] and the other the conjugate base dissociation, or SN1 CB mechanism.[2] In water solvent the two mechanisms give rise to the same product, since the intermediate in the conjugate base mechanism would react with the solvent to yield a hydroxo product. However in a non-hydroxylic solvent different products are predicted for the two mechanisms in the event that an excess of some nucleophilic reagent other than hydroxide ion or water is present.

We wish to report some results which are easily explained by the SN1 CB mechanism and cannot be explained by the SN2 mechanism. The solvent used is dry dimethylsulfoxide. As examples of a large number of similar experiments with various cobalt(III) complexes and nucleophilic reagents, these reactions illustrate the chief points. Spectral data were used to follow the reactions and identify the reaction products.

$$\underset{0.001\ M}{trans\text{-}Co(en)_2NO_2Cl^+} + \underset{0.01\text{–}0.10\ M}{NO_2^-} \longrightarrow Co(en)_2(NO_2)_2^+ + Cl^- \quad (1)$$

$$\underset{0.001\ M}{trans\text{-}Co(en)_2NO_2Cl^+} + \underset{0.001\ M\text{ or less}}{OH^-} \longrightarrow Co(en)_2NO_2OH^+ + Cl^- \quad (2)$$

$$\underset{0.001\ M}{trans\text{-}Co(en)_2NO_2Cl^+} + \underset{0.10\ M}{NO_2^-} + \underset{0.001\ M}{OH^-} \longrightarrow Co(en)_2(NO_2)_2^+ + Cl^- + OH^- \quad (3)$$

$$\underset{0.001\ M}{Co(en)_2(NO_2)(OH)^+} + \underset{0.10\ M}{NO_2^-} \longrightarrow \text{indefinite product, some } Co(en)_2(NO_2)_2^+ \quad (4)$$

Reaction (1) shows first order kinetics and has a half-life of 5–6 hr., nearly independent of the nitrite ion concentration. Reaction (2) is very fast, being complete in less than 2 min. when the first reading was made. Reaction (3) is also complete in less than 2 min. yet the product is cleanly the dinitro complex. Reaction (4) is very much slower than (2) or (3) and gives a spectrum lacking sharp bands which steadily changes over several days.

The following points are also significant: Only catalytic quantities (10%) of hydroxide ion are required to cause a rapid reaction of the cobalt(III)

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[1] D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953); C. K. Ingold, Fifth Weizmann Memorial Lecture Series, the Weizmann Science Press of Israel, 1959.

[2] F. J. Garrick, *Nature*, **139**, 507 (1937); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons Inc., New York, N. Y. 1958, pp. 124–132.