coupling interaction arises from sigma–pi exchange terms in the Hamiltonian operator. Recognition of the correspondence between these exchange terms and those occurring in related pi-electron radicals[8] makes possible a considerable simplification of the theory. Although the general result obtained by this procedure is still rather complicated, a number of approximations permit the pi-electron contribution $A_{\mathrm{HH}'}(\pi)$ to be written in the very simple form

$$A_{\mathrm{HH}'}(\pi) = K \sum_{T} \frac{a_{\mathrm{H}}(T)a_{\mathrm{H}'}(T)}{\Delta\pi(T)} \qquad (1)$$

Here $a_{\mathrm{H}}(T)$ and $a_{\mathrm{H}}'(T)$ are the hyperfine splitting constants for the pair of pi-electron radical fragments that correspond to the triplet state T and $\Delta\pi(T)$ is the singlet–triplet transition energy. The sum in Eq. (1) is over all the pi-electron triplets T that make a significant contribution. If $A_{\mathrm{HH}'}(\pi)$, $a_{\mathrm{H}}(T)$, and $a_{\mathrm{H}}'(T)$ are expressed in c.p.s. and $\Delta\pi(T)$ in eV., the constant K is equal to 2.1×10^{-15}.

To clarify Eq. (1), we consider a simple application. The 1,3-proton coupling in propylene can be estimated by including only the lowest pi-electron triplet state. This state corresponds to the two radical fragments H–$\dot{\mathrm{C}}$ and H–C–$\dot{\mathrm{C}}$ for which hyperfine splitting constants a_{H} of -65×10^{6} c.p.s.[9] and $+75 \times 10^{6}$ c.p.s.,[10] respectively, are appropriate. With the transition energy $\Delta\pi(T)$ set equal to 6 e.V., the most likely value for ethylene,[11] a value of −1.7 c.p.s., is obtained for $A_{\mathrm{HH}'}(\pi)$.

TABLE I

PROTON SPIN COUPLING CONSTANTS

Proton linkage	$A_{\mathrm{HH}'}(\pi)$ (c.p.s.) (theor.)	$A_{\mathrm{HH}'}$ (c.p.s.) (exp.)
H—C=C—C—H	−1.7	−1.4 to −1.8[1]
H—C=C=C—H	−6.7	6.1 to 7.0 (unknown sign)[2]
H—C—C=C—C—H	+2.0	1.2 to 1.5 (unknown sign)[3]
H—C=C=C=C—H	+7.8	Not measured

Substitution of available values for the hyperfine constants and triplet state energies into Eq. (1) yields the results given in Table I. Only systems containing a double bond with the protons separated by three or four carbon atoms have been included. Where possible the absolute signs of the theoretical results are compared with the relative signs obtained by the analysis of n.m.r. spectra.[12] It is seen that the calculated values for the coupling constants are in agreement with the available experimental measurements. The large value predicted for butatriene has yet to be verified, as do the signs in several of the systems for which only the magnitudes are available.

From the theory presented in this paper it is evident that the pi electrons provide the dominant contribution to the coupling constant in certain unsaturated molecules. Corresponding results are found for similar couplings in systems that contain a triple bond (*e.g.*, methylacetylene). A more detailed discussion of the theoretical development leading to Eq. (1) and other applications are to be published in the *Journal of Chemical Physics.*

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[8] See H. M. McConnell, *J. Mol. Spect.*, **1**, 11 (1957); *J. Chem. Phys.*, **30**, 126 (1959), for a corresponding device applied to aromatic molecules.

[9] H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); H. S. Jarret, *ibid.*, **25**, 1289 (1956); M. Karplus, *ibid.*, **30**, 15 (1959).

[10] R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956); A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

[11] W. J. Potts, Jr., *J. Chem. Phys.*, **23**, 65 (1955).

[12] The theoretical sign of A_{HH} is defined as positive if the nuclear spin state with the proton spins paired is of lower energy. The experimental sign is relative to the HCCH coupling, which is taken to be positive.

UNSPECIFIC TRITIUM LABELLING ACCELERATED BY MICROWAVE, ALTERNATING CURRENT AND DIRECT CURRENT ELECTRICAL DISCHARGES AND BY ULTRAVIOLET RADIATION

Sir:

In a recent publication Westermark, *et al.*,[1] presented electrical discharges for accelerating unspecific labelling. Systematic studies based on high frequency (2425 mc./sec.) microwave discharge, low frequency glow discharges and ultraviolet radiation have now been performed on a variety of organic substances ranging from high polymeric substances of known characteristics to liquids of low boiling points.

A short record of some findings will be given. Detailed experimental techniques and discussions will be published elsewhere.[2]

Most of the radioactivity measurements were made in an Ekco liquid scintillation counter. Polystyrene and polymethyl methacrylate were purified by precipitating in excess of ice-cooled methanol, and then filtering and drying at 80° for 24 hr. Tritium was supplied in small ampoules with fragile hook seals from the Radiochemical Centre, Amersham.

With polystyrene (200 mg.) and 50–100 mC. of tritium in evacuated Pyrex tubes under microwave discharge in a silver plated brass cavity, specific activities of about 100 mC./g. in the purified product were reached for an energy input of about 5000 watt sec. The percentage of tritium fixed was about 10–20% and the yield of fixation 0.002 mC./watt sec. This activity tended to decrease at higher energy inputs. The pressure of tritium was found to decrease with energy unless too much energy was put in. There was no difference between the labelled material and the original polystyrene in the ultraviolet absorption spectra taken over a wide range of wave lengths. In an experiment with 20 mg. placed 2.5 cm. away from the plasma region in a bent section of the tube, the tritium pressure decreased more slowly but the activity finally obtained was 426 mC./g.; typical treatment time was 1660 sec. This result suggests that tritiation occurs via T atoms as it is not probable that significant amounts of gaseous ions would reach the material under the above conditions. Further evidence in favor of this hypothesis is given below. Except for the effect of reflected photons the bent-tube method eliminates the destruction of organic material from short wave length ultraviolet light from the plasma zone.

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[1] T. Westermark, H. Lindroth and B. Enander, *J. Appl. Radiation and Isotopes*, **7**:**4**, 331 (1960).

[2] N. A. Ghanem and T. Westermark, paper to be presented before the I.A.E.A. isotope conference in Copenhagen, Sept., 1960.

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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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).