Letters to the Editor

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Direct Introduction of Deuterium into Benzene without Heterogeneous Catalysis

THE transference of deuterium to benzene from hydrogen gas or from water at the surface of finely divided metal catalysts has been realised by Horiuti, Polanyi and Ogden[1], and unsuccessful attempts to achieve a similar object have recently been recorded by Farkas, Farkas and Rideal[2] and Murray, Squire and Andrews[3].

We are studying the direct introduction of deuterium into the aromatic nucleus by means of ordinary electrophilic reagents, that is, without heterogeneous catalysis, and it may be of interest if some of our results for benzene itself are set out for comparison with the above catalytic studies.

The reagent employed for the introduction of deuterium into this hydrocarbon was concentrated aqueous sulphuric acid. It was prepared from sulphur trioxide and the appropriate quantity of heavy water. When benzene was treated with anhydrous sulphuric acid extensive sulphonation took place, but this was largely avoided by the use of 90 per cent acid. When the latter acid and benzene were brought together hydrogen exchange readily occurred.

Quantities of benzene and aqueous acid each containing the same number of atoms of hydrogen ($\frac{1}{3}C_6H_6 + H_2O + xSO_3$) were shaken together for various periods at the room temperature. The benzene was neutralised, dried and burnt, and the density of the combustion-water was determined. When the sulphuric acid had the ordinary hydrogen-isotope ratio the combustion-water had the same density as ordinary water to within the accuracy of the density measurements (1 in 10^6). When, however, the acid had an enhanced deuterium content, a part of this isotope became transferred to the benzene, which on combustion yielded heavy water. For times of shaking up to 24 hours the proportion of deuterium thus transferred increased with the time. The following two experiments with a specimen of 90 per cent sulphuric acid prepared from water having a density of 2,149 parts per million above normal will give an idea of the velocity of the exchange (the equilibrium constant is being determined) :—

Time of shaking (hours)	Excess density in p.p.m. of	
	H_2O of residual ($H_2O + xSO_3$). By diff.	Combustion H_2O from C_6H_6
3	2060	89
24	1199	950

Results will later be reported showing that certain substitution products of benzene undergo spontaneous exchange of their nuclear hydrogen atoms with the hydrogen of water or acids much more readily than does benzene itself.

It is well known that the familiar substitution effects of reagents such as sulphuric acid require the assumption of 'abnormal' polarisation, that is, polarisation in a direction contrary to that of the ordinary ionisation of the reagent (for example, $\overset{\delta-}{OH}\leftarrow\overset{\delta+}{SO_3H}$). The existence of an aromatic substitution dependent on 'normal' polarisation ($\overset{\delta+}{H}\rightarrow\overset{\delta-}{SO_4H}$), that is, one corresponding to the ionisation, is here demonstrated for the first time. Evidently the reaction is facile, though undetectable except by the use of an isotopic indicator.

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[1] *Trans. Faraday Soc.*, **30**, 663 ; 1934. Cf. NATURE, **134**, 377, Sept. 8, 1934.
[2] *Proc. Roy. Soc.*, A, **146**, 639 ; 1934.
[3] *J. Chem. Phys.*, **2**, 714 ; 1934.

Composition of Cosmic Rays

THE new information regarding the absorption of high energy photons and electrons, presented at the recent International Congress on Nuclear Physics, suggests an improved interpretation of certain cosmic ray phenomena. Three distinct components of cosmic rays have been recognised. Eckart's analysis[1] of the depth *v.* ionisation data shows clearly the presence of two components in the cosmic rays which reach the earth's surface. These components have mean absorption coefficients of about 0·6 and 0·06 respectively per metre of water. Gross[2] and Compton and Stephenson[3] find that the high altitude data from stratosphere balloons also indicate the presence of two components, the more penetrating of which is probably identical with Eckart's less penetrating component. Let us call these components *A*, *B* and *C* in the order of their penetrating power.

Following the theories of Størmer, Lemaître and Vallarta, and others, we can calculate the minimum energies of electrons, protons and alpha particles which reach the earth at a given latitude through the earth's magnetic field. Corresponding to these minimum energies, there will be minimum ranges in the atmosphere. Component *A*, which is relatively most prominent near the top of the atmosphere, is affected less by the earth's magnetic field than component *B*. Its penetration corresponds either to the range of alpha particles capable of traversing the barrier of the earth's magnetic field, or to photons with the absorption coefficient of the shower producing radiation.* Our approximate calculations show a close correspondence between electron ranges†

* This suggestion of photons for component *A* has been put forward by P. M. S. Blackett, because of the close correspondence between its rate of absorption and that observed for the shower-producing radiation, which seems to consist of photons. It is also doubtful whether alpha particles could retain their integrity with kinetic energies hundreds of times greater than that (3×10^7 electron volts) with which they are bound together. Compton and Stephenson found the assumption of either photons or alpha particles to be consistent with their high altitude data. A comparison of the new high altitude ionisation measurements of Bowen, Millikan and Neher, with the earlier ones of Regener and Piccard at slightly lower magnetic latitudes, however, suggests an effect on this component due to the earth's magnetic field. This would require a charged particle rather than a photon composition. High altitude measurements now under way at lower magnetic latitudes, where the effect of the earth's field is greater, should serve to distinguish between the alpha particle and the photon hypotheses.

† Using a less complete theory, Compton and Stephenson[3] calculated that the electrons would have slightly greater penetration than the protons. The new results, which take into account the radiation excited by the particles on traversing matter, make their component *B* correspond to positrons rather than to the protons which their calculation favoured.