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, $\overset{\delta-}{\mathrm{OH}}\leftarrow\overset{\delta+}{\mathrm{SO_3H}}$). The existence of an aromatic substitution dependent on 'normal' polarisation ($\overset{\delta+}{\mathrm{H}}\rightarrow\overset{\delta-}{\mathrm{SO_4H}}$), 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.

and component B. The minimum ranges for protons penetrating the magnetic barrier should be greater than for electrons, which suggests identifying protons with component C, though the presence of the strong component B prevents using existing depth-ionisation data to make this identification definite. These comparisons will be given in detail elsewhere. We wish here to point out that if component B is identified with electrons (positrons or negatrons), and C with protons, certain cosmic ray phenomena find a simple explanation.

Recent theoretical studies have shown that for the very high energies involved in cosmic rays, the probability that electrons shall lose energy by photon excitation increases rapidly with the energy, and should represent the most important method of energy dissipation. This deduction is supported by Anderson and Neddermeyer's measurements of electron energy losses, as reported to the Congress. For protons, however, the theory indicates that energy losses by photon excitation should be of negligible importance. This difference between the action of electrons and protons would account for the higher absorbability of the former, assuming that both types of particles have roughly the same distribution of energies. An equally important difference is that the electrons will form a prolific source of secondary radiation, showers, etc., whereas the protons should be accompanied by relatively feeble secondary rays. Component B should thus be the primary 'shower-producing radiation'.

The increasing importance of component B as compared with C at higher altitudes must accordingly result in an increased proportion of secondary radiation. We would thus explain the following phenomena :

1. The increasing importance of the transition effect at higher altitudes, as found by surrounding an ionisation chamber with several centimetres of lead.*

2. Rossi's new observation, as reported at the Congress, that the ratio of the frequency of showers to the frequency of coincidences increases at high altitudes (up to 3,500 metres).

If protons require less energy to penetrate the atmosphere than do electrons, the slowest protons reaching sea level had initially, at the top of the atmosphere, less energy than the slowest electrons. Therefore the protons should be more affected by the earth's magnetic field than the electrons, because they had less energy and therefore smaller mass when under the influence of the field. This would mean that at a given level the penetrating component C should show stronger magnetic effects than component B and its secondary radiation. Rossi has measured the difference between the number of rays coming from the west as compared with the east, at 45° zenith angle, and found this difference to be greater for the rays penetrating 8 cm. of lead than for the total radiation. Also, Johnson's measurement of the shower-producing radiation, using three counters not in line, showed a smaller west-east difference than that for the coincidence-producing radiation. This phenomenon is likewise explicable if it is the electrons of high initial energy which produce the showers, whereas the initially slower non-radiating protons which contribute to the coincidences are more easily deflected by the earth's field.

There is another possible reason why the electrons (and therefore the showers) show a smaller east-west effect than the protons (and therefore the total *primary* radiation): It may be that component B consists of negatrons as well as positrons, whereas component C contains only particles of positive charge, namely, protons. Johnson's observations at high altitudes in Peru that more rays come from the west than from north or south, however, is difficult to reconcile with any negatively charged particles prevented from reaching the earth by the field there used. This points to the conclusion that the electron component of cosmic rays consists at least predominantly of positrons.

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[1] C. Eckart, *Phys. Rev.*, **45**, 851 ; 1934.
[2] B. Gross, *Z. Phys.*, **83**, 217 ; 1933.
[3] A. H. Compton and R. J. Stephenson, **45**, 441 ; 1934.

* Cf., for example, A. H. Compton (*Phys. Rev.*, **43**, 387 ; 1933) whose curve *a*, Fig. 3, shows the increase with increasing altitude of the fraction of the cosmic rays removed by 2·5 cm. of lead.

Secondary Emission from Elements Bombarded with Neutrons

WE have measured the absorption of the complex radiations from Po + Be in various elements, using a Geiger-Müller counter as a detector. The source of Po + Be (3·5 mc.) was enclosed in a glass tube and shielded with a cylinder of lead 2·5 cm. in thickness. The walls of the counter, which was placed 12 cm. from the source, were of aluminium, 0·18 mm. thick. The absorbing material was in the form of large slabs placed between the source and the counter. The following results have been obtained :

	C	Al	Fe	Zn	Sn	Sb	Ba	Hg	Pb
At. Weight	12	27	54	64	120	122	138	201	208
μ in cm.$^{-1}$	0·050	0·095	0·195	0·182	(0·00)	(0·06)	0·098	0·279	0·300
H/ρ in cm.^{2} gm.$^{-1}$	0·034	0·037	0·025	0·025	(0·00)	(0·010)	0·026	0·021	0·026

It is seen that tin shows no detectable absorption ; antimony, which follows tin in the periodic system, shows an abnormally low absorption. A plate of lead, 8 mm. in thickness, interposed between the absorbing screen and the counter, reduced the number of kicks to half. It would appear, then, that the apparent low absorption in tin and antimony is to be ascribed to more absorbable secondary radiations produced by the passage of the primary rays through these elements. It seems probable that the softer radiations are of the nature of γ-rays, and arise from excitation of nuclear levels of elements near tin in the periodic table. It will be necessary to use stronger sources of neutrons and a modified technique in order to investigate these secondary soft radiations in greater detail, and we hope shortly to be able to report more fully on their nature.

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IN the course of observations of the neutrons produced by the bombardment of elements with