this mode of ortho-para substitution, in which both a molecule of the nitro-compound and the ion suffer loss of an electron to another agent, and to which similar considerations in regard to ortho- or parasubstitution are applicable.

Whereas such substitution of nitrobenzene arises in general from activation of the nitro group by an agent which later becomes a substituent, ordinary meta-substitution, so far as it is due to activation9, depends on that of an external agent, for example, by hydrogen bond formation. Meta-substitution is thus related to  $\alpha$ -activation of carbonyl compounds by acids. If, however, an  $\alpha\beta$ -unsaturated carbonyl derivative be activated by mercuric ion, we have the following changes:

Although this case is closely related to the mercuration of nitrobenzene, there is here no need for proton extrusion, since the radical ion can achieve neutrality by accepting an anion A- from the surrounding medium. Consequently the relative sites of mercuration are different in the two cases. Initial activation by cupric ion would generate cuprous ion which, as Waters has recognized, will in turn liberate from diazonium ion phenyl radical for arylation corresponding to the mercuration just discussed.

We need thus only speak of the 'new' organic chemistry in the sense that we enlarge the present relatively limited outlook to one exhibiting more explicit recognition of the relation of chemical reaction to processes of oxidation and reduction. Indeed, the formulation of chemistry in general needs a similar revision. Thus, we have as examples from inorganic chemistry related to those above, the substitutive mercuration of ammonia in the formation of Nessler's reagent, and the colour of those metallic compounds which do not contain coloured cations. The colour of mercuric oxide, for example, is presumably due to a relationship in its lattice which we may represent

$$\mathrm{Hg} \cdot \mathrm{O}'' \rightleftharpoons \mathrm{Hg} \cdot \mathrm{O}'.$$
 A kinetic study of the nitrosation of dimethylaniline,

carried out in conjunction with Dr. G. Baddeley and Mr. D. M. Lever, having revealed a similar accelerative influence of chloride ions to that observed in the case of diazotization, we have shown that a nitrosating reagent, with [H'], [Cl'] and [HNO<sub>3</sub>] respectively 0.2, 1.9 and 0.1 molar, slowly dissolves metallic gold at the ordinary temperature, while solutions of benzene, ethyl benzene and tetralin in glacial acetic cid saturated with hydrogen chloride and containing a molar concentration of nitrous acid at 25° furnish small yields of chlorobenzene, 4-chloroethylbenzene and a mixture of ac- and ar-chloro-derivatives respectively. In other words, we have in the reagent

$$HNO_2 + H' + Cl' \rightleftharpoons H_2O + NO + Cl$$
,

corresponding to the familiar reaction with iodide ion, and the acceleration noted above is due to atomic chlorine or to nitrosyl chloride, according as one regards the latter11.

A kinetic study with Dr. G. Baddeley has shown that the rate of formation of 4:4'-diethoxy-1:1'dinaphthyl from a-ethoxynaphthalene in presence of nitrobenzene and aluminium chloride is proportional to the concentration of the ethoxy-derivative. It thus involves the corresponding radical<sup>11</sup>. It is illustrative of the theme developed at the outset of this note that the course of the reaction is essentially that of benzene substitution as formulated above.

It seems to have been overlooked that olefinic α-oxidation was established so far back

as 1894 when Wagner demonstrated

the structure of sobrerol.

Studying the use of tertiary butylhypochlorite as a chlorinating agent, Dr. R. F. Garwood and I have shown it to (a) attack carbonyl compounds instantly, especially in presence of a trace of aluminium chloride, boron trifluoride, etc., forming, for example, mono- and di-chloroethyl malonates from ethyl malonate; (b) furnish a 65 per cent yield of \( \Delta \cdot cyclo-hexenyl \) chloride from cyclohexene under Ziegler's chlorination conditions. Also, independently following this up, Dr. Garwood has demonstrated the efficiency

of this reagent in presence of benzoyl peroxide in chlorinating toluene, ethyl benzene, p-bromotoluene and cyclo-hexane to benzyl chloride, α-phenylethyl chloride, para-bromobenzyl chloride, and cyclohexyl chloride respectively. Further, in contrast to the experience of Kharasch and Brown, using sulphuryl chloride and benzoyl peroxide, even para-nitrotoluene furnished some para-nitrobenzyl chloride.

It is obvious that fuller treatment of these various matters is required, and it is hoped to provide these in due course.

- <sup>1</sup> Dimroth, Ber., 35, 2036 (1912).
- Billmann, Ber., 43, 568 (1910); Schrauth and others, ibid., 695; 44, 1048, 1432 (1911).
- Meerwein, Buchner and Emster, J. prakt. Chem., 152, 237 (1939).
- <sup>4</sup> Compare Garwood and Kenner, J. Soc. Chem. Ind., 62, 166 (1943). <sup>8</sup> Chem. Rev., 15, 225 (1934).
- Institute of Chemistry (London, 1932).
- J. Chem. Soc., 220 (1941).
- \* Ann., 428, 76.
- <sup>9</sup> Compare Hughes and Ingold, J. Chem. Soc., 608 (1941).

- Jones and Kenner, J. Chem. Soc., 1848 (1931); 711 (1932).
  Kenner, Chem. and Ind., 469 (1933).
  Compare Hollemann, "Direkte Einfuhrung von Substituenten in den Benzolkern" (Leipzig, 1920), 199.
  Wall Br. 20, 242 (1992).
- 18 Wohl, Ber., 32, 3468 (1899).
- 14 Compare Lobry de Bruyn, Rec. trav. chim., 23, 39 (1901).
- 15 Montmollin, Helv. Chim. Acta, 6, 94 (1923).

## GAS RESEARCH BOARD

THE Gas Research Board—now responsible for the research activities of the British gas industry—has issued its fifth annual report (Gas Research Board, I Grosvenor Place, London, S.W.1), covering the session ending June 30, 1944. With the end of hostilities in Europe it has become possible to disclose some of the war-time activities.

Work on the gasification of coal in hydrogen under pressure had, by that time, passed from the laboratory

into the works as a result of the installation of a small plant in the Bournemouth gasworks. In the initial stages a semi-coke, heated to 600° C., was treated with hydrogen under 50 atmospheres pressure. Under these conditions, gasification partly by liberation of volatile matter and partly by reaction of hydrogen with carbon takes place with great rapidity, for the formation of methane is an exothermic reaction. Another approach to the production of methane from coal is the synthesis from mixtures of carbon monoxide and hydrogen. Synthesis of liquid hydrocarbons is better known, but by choice of catalyst and conditions methane can also be obtained. The most important of the conditions is the almost complete removal of organic sulphur from the gas by processes which require very stable catalysts. Results of high promise have been obtained and suggest that fuel gas may soon be distributed almost free from sulphur.

All this work aims at the preparation of a fuel gas without the limitation of starting from high-class coking coal, rather indeed from any coal. This achievement will almost certainly be accompanied by

the production of gas from sulphur.

In recent years it has been recognized that although heat is transferred by convection and radiation, the differentiation of the two may be important. In certain operations, especially those involving drying, radiation may prove more effective than convection. Effectiveness may be influenced by the quality not only of the source of radiation but also by that of the surface receiving the radiation. The report shows that the Gas Research Board is actively engaged in this field because gas-heated surfaces are specially effective for radiant heating, and this promises great industrial application.

Another branch of the Board's activities involves the separation by refrigeration of coal gas into its constituent gases, whereby advantage can be gained

from the special properties of each.

The report shows that the Board, in spite of wartime difficulties, is making rapid progress in the development of new techniques for the manufacture and use of gaseous fuel.

## FREQUENCY OF EARTHQUAKES IN CALIFORNIA

A CCORDING to Gutenberg and Richter, the southern California area, including the Owens Valley, has about one half of one per cent of the seismic activity of the globe ("Frequency of Earthquakes in California." By B. Gutenberg and C. F. Richter. Bull. Seis. Soc. Amer., 34, No. 4, 185; 1944). This conclusion is arrived at by considering statistically up-to-date information concerning earthquakes, employing the instrumental magnitude scale.

The magnitude M of an earthquake was originally defined as proportional to the logarithm of the maximum trace amplitude on the seismogram of a standard torsion seismometer distant 100 km. from the epicentre, and having a normal shallow depth. The magnitude scale is chosen to make M=0 correspond to the smallest instrumentally recorded shocks. It is found that M=2 corresponds to the smallest shocks ordinarily reported felt,  $M=4\cdot5$  causes slight damage, M=6 earthquakes are moderately destructive, and  $M=8\cdot5$  corresponds to the largest recorded shocks.

Since 1921, the following shocks in the California-Nevada region have had magnitude 7 or greater: Jan. 31, 1922 (7·3), off the north coast; Jan. 22, 1923 (7·1), off the north coast; Nov. 4, 1927 (7·0), off Point Arguello; Dec. 20, 1932 (7·3), west-central Nevada; Dec. 31, 1934 (7·0), south of the Imperial Valley. In the present century, two shocks in the same region have exceeded magnitude 7·5: April 18, 1906 (8·25), central California; Oct. 2, 1915 (7·75), north-central Nevada.

This gives the California-Nevada region about 90 per cent of the seismic activity of the United States.

According to the authors, the expected occurrence of about four great earthquakes per century in the California region by no means excludes the possibility that double that number might occur in a given century, or that a whole century might pass without even one. Further, the events are not strictly independent. A great shock, such as that of 1906, represents a regional release of strain; after the immediate aftershocks have subsided, it may be expected to be followed by a period of abnormal quiet, as is probably now the condition in central California. It is worth noting that great shocks are to be looked for only in association with the major active faults and structures, such as the San Andreas fault zone and the trough of the Owens Valley. The other faults and active structures are characterized at most by moderately destructive earthquakes like those at Santa Barbara and Long Beach.

## THE STONE AGE IN EAST AFRICA

IMMEDIATELY before the War, industries belonging to a so-called Tumbian culture were being recognized at many sites in eastern and western Africa. First noticed by Dr. X. Stainer in the Congo, industries of similar types were soon being identified in many other areas. Dr. Menghin and T. P. O'Brien (in his book on the prehistory of Uganda) went so far as to suggest that the Tumbian culture was derived directly from that of the coups de poing makers, that it could be described as a sort of Acheulean gone to seed. Prof. H. Breuil, however, in a recent study of Dr. Cabu's finds, denies the existence of the Tumbian as a distinct culture, and he and Prof. van Riet Lowe suggest that the industries represent only a variation of the Sangoan culture of Uganda with strong Fauresmith affinities (Trans. Roy. Soc. of South Africa, 30, pt. ii; 1944).

Dr. Leakey and Archdeacon Owen have now entered the ring, and in the first Occasional Paper of the Coryndon Memorial Museum, entitled "A Contribution to the Study of the Tumbian Culture in East Africa", they unequivocally uphold its status as a culture. Owen and Leakey's publication deals mainly with a series of sites, chiefly from the Kavirondo area, where industries belonging to various stages of this debatable culture have been discovered. There are several pages of illustrations. In conclusion, there is a general discussion on certain aspects of the Stone Age in Kenya, followed by an appendix, where Breuil and Lowe's work, quoted above, is cited, and the conclusions there set out denied.

As a personal opinion I can only add that every so-called Tumbian assemblage of implements which I have seen has appeared to contain several elements and to have been a mixture of the relics of more than