numbers can be calculated in terms of the density and surface tension of the liquid. Thus many of the results obtained by Band and his collaborators[3] may be immediately recast in the present dissociation treatment.

TSE-PEI TSENG

Physics Department,
Yenching University in Chengtu,
Chengtu, China. May 8.

---

[1] Fürth, *Proc. Camb. Phil. Soc.*, **37**, 252 (1941).

[2] Auluck and Kothari, *Proc. Camb. Phil. Soc.*, **41**, 181 (1945).

[3] Ch'eng, Tseng, Feng and Band, *J. Chem. Phys.*, **9**, 123 (1941).

Unitary Theory of Hydrocarbon Catalytic Reactions

IN the course of the investigation of the catalytic isomerization of butene-1 to butene-2, we have been led to a formulation of such diverse hydrocarbon reactions as the double-bond migration, alkylation, polymerization, and cracking in terms of one mechanism. The experimental facts on which this view is based are as follows.

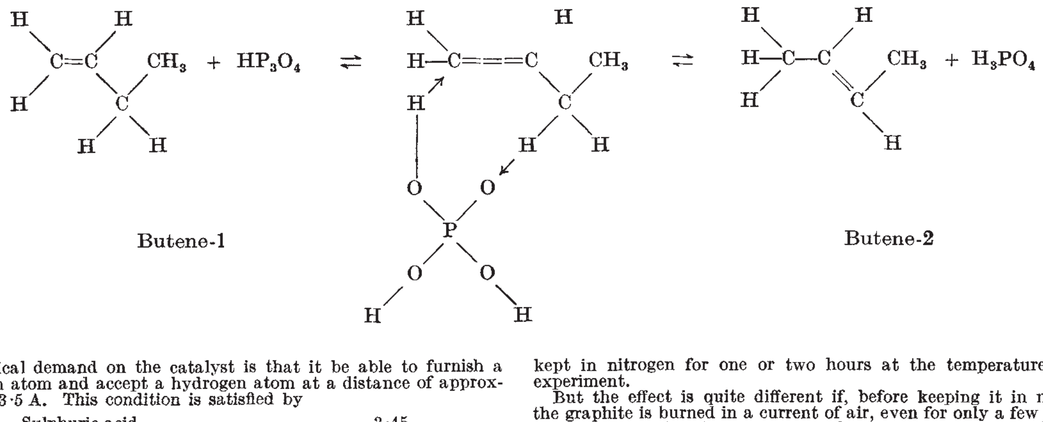
The isomerization of butene-1 was studied using phosphoric acid. The rate was found to be proportional to the pressure of the butene and to the amount of phosphoric acid. The activation energy decreased with increasing phosphorus pentoxide content from 16 kcal. for 70 per cent P_2O_5 to 7·8 kcal. for 97 per cent P_2O_5.

The change of radioactive tritium from radioactive phosphoric acid to butene-1 was studied at the same time. Whereas the activation energy for the isomerization reaction for this concentration of acid was 14·5 kcal., that for the exchange reaction was 17·8 kcal. The rate of exchange at 27° C. was slower than the rate of isomerization, the difference corresponding to a difference in activation energies of 3 kcal. This is in good agreement with the difference obtained from the temperature coefficient of the two processes. Thus, these two processes seem to follow the same mechanism, the difference in the rate being due to the difference in the zero point energies of hydrogen and tritium bonds.

Furthermore, it was found that radioactive water T_2O, and radioactive hydrochloric acid TCl, did not exchange with butene. On the other hand, tritium phosphoric acid did *not* exchange with ethylene but did exchange with propylene.

These experimental findings suggest that the catalytic isomerization of the double bond in the butenes is not due to the addition of a proton to the double bond with formation of a carbonium ion, but must involve another mechanism. We wish to propose the following 'hydrogen transfer' mechanism, which is consistent with the above experimental results and which is based on spacial inter-relationships of catalyst and substrate.

When a phosphoric acid molecule approaches a butene-1 molecule, the approach is postulated to take place in such a way that one of the hydrogen atoms of the phosphoric acid approaches the end carbon atom, while the oxygen having no hydrogen on it approaches the hydrogen atom on the third carbon atom in the butene-1 molecule. It is found by molecular models that there will be a good fit between the phosphoric acid and the butene. When the phosphoric acid breaks away from this complex, it may take with it the hydrogen atom from the third carbon atom and leave a hydrogen atom on the first carbon atom. The result is butene-2.



The critical demand on the catalyst is that it be able to furnish a hydrogen atom and accept a hydrogen atom at a distance of approximately 3·5 A. This condition is satisfied by

Sulphuric acid	3·45
Phosphoric acid	3·46
Silicic acid	3·50
Perchloric acid	3·41
Wet $AlCl_3$ ($HAlCl_4$)	3·46
Partially hydrogenated nickel	3·52

Polymerization of hydrocarbons is visualized according to this mechanism as the hydrogen transfer between two olefins. Alkylation is formulated as a hydrogen transfer from a paraffin to an olefin. Finally, cracking is formulated as the reverse of alkylation. The carbon-carbon bond is broken as the catalyst (alumino-silicic acid) removes the hydrogen from one carbon and transfers it to a carbon atom one removed from the first.

JOHN TURKEVICH
ROBERT K. SMITH

Frick Chemical Laboratory,
Princeton University.
May 16.

Mechanism of the Combustion of Graphite

THE following experiments provide a new understanding of the so-called 'surface oxides' to which the essential role in the mechanism of the oxidation of carbon has long been attributed[1].

The experiments were carried out with very finely powdered Acheson graphite of ash content 0·24 per cent (SiO_2, Al_2O_3, Fe_2O_3, CaO and traces of Ti, V, Mg, Co, Cu). The sample was degassed *in vacuo* at 900° C. and kept over sulphuric acid *in vacuo*. The speed of combustion is measured by the removal and estimation of the reaction products, carbon monoxide and dioxide, formed during 15 minutes at 510° C. This speed is expressed conventionally by the mass of carbon gasified during the sampling.

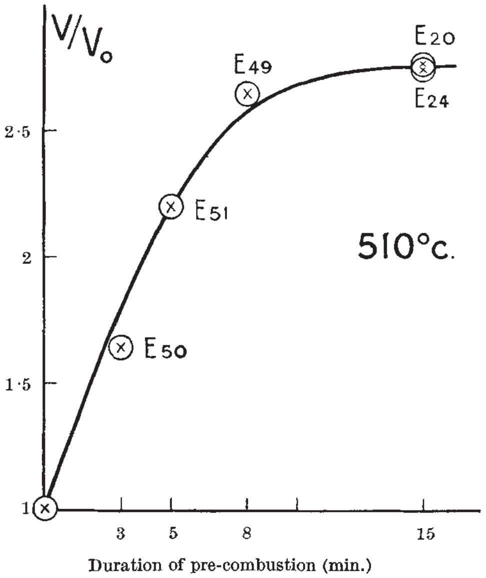


Fig. 1. TIME IN NITROGEN, 1 HR.

The method permits the measurement of a speed V_0 which is reasonably reproducible ($V_0 = 2·35 \pm 0·15$ mgm./min.), and which does not vary with the duration of combustion. As one might expect, the speed remains the same if, before the run, the graphite sample is kept in nitrogen for one or two hours at the temperature of the experiment.

But the effect is quite different if, before keeping it in nitrogen, the graphite is burned in a current of air, even for only a few minutes (pre-combustion). The curves show the ratio V/V_0 (V being the speed of combustion after treatment) either as a function of the duration of pre-combustion (for one hour of immediately subsequent treatment in nitrogen; see Fig. 1) or as a function of the length of stay in nitrogen (for 15 minutes of pre-combustion; see full curve in Fig. 2). It is clear that the contact of hot graphite and oxygen can cause an important stepping-up of the combustibility of graphite if the 'surface oxide' which forms has time to develop protected from the air.

After 'maturing' in nitrogen, not only does the graphite burn more quickly but it also burns more completely; for example, 8–10 per cent of carbon monoxide in the mixture carbon monoxide and dioxide in experiments *E* 20, *E* 24, *E* 33, instead of 23·5 per cent for the experiments performed on non-treated graphite. This state of high combustibility is destroyed little by little during the combustion. Sampling after the 'activated' graphite has burned continuously for 30 minutes shows that the speed of combustion is only 82 per cent of that at the commencement (experiments *E* 56, *E* 21, *E* 25, *E* 34; dotted curve in Fig. 2).