

Received December 20, 1973.

¹ Macpherson, P. B., and Cameron, A., *ASLE Trans.*, **16**, 68-72 (1973).

² Johnson, L. G., *The statistical treatment of fatigue experiments*, (Elsevier, Amsterdam, 1964).

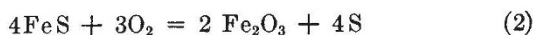
³ Zaretsky, E. V., Anderson, W. J., and Parker, R. J., *ASLE Trans.*, **5**, 210-219 (1962).

Is pyrophoric iron sulphide a possible source of ignition?

THERE are many practical environments in which iron oxide, in the form of surface rust, may be exposed to atmospheres containing hydrogen sulphide at various concentrations. Gas lines, chemical plant, distillation units, crude-oil cargo and storage tanks are examples.

We wish to draw attention to the hazard that can arise in such situations because of the formation of pyrophoric iron sulphide, and the possibility that it may act as a source of ignition for inflammable vapours.

The reactions involved in the formation of iron sulphide and its subsequent oxidation on exposure to atmosphere may be represented in a simplified form as follows



Both reactions are exothermic, the ΔH° values for reactions (1) and (2), based on 2 FeS, being about -40 and -151 kcalorie (-168 and -635 kJ) respectively. If reaction (2) can proceed rapidly and with little dissipation of heat, high temperatures can be expected in the material.

We have found that the reactivity of iron sulphide depends on the type of iron oxide from which it is derived. For example, a common form of rust (α -FeOOH) yields on exposure to hydrogen sulphide a material which is particularly reactive. When exposed to air at ambient temperature, the material oxidizes so rapidly that surface glowing and sparking can be seen within seconds. If inflammable vapours come into contact with the material in this condition, the material can act as a source of ignition. We suspect that several recent minor explosions in the cargo tanks of crude-oil tankers may have been caused in this manner. This view is reinforced by the fact that we have been able to demonstrate that pyrophoric iron sulphide can form at partial pressures of hydrogen sulphide corresponding to the values encountered in the ullage regions of crude-oil cargo tanks.

It is fortuitous that in practical situations not all sulphidated iron oxide is as reactive as the material described. The reactivity can be influenced by a number of factors. For instance, the progressive buildup of sulphur generated during each sulphidation/oxidation cycle can exert a 'screening' effect, resulting in reduced reactivity of the sulphide so formed. Particle geometry and the presence of occluded materials can also affect reactivity.

Although pyrophoric iron sulphide has, of course, been known for many years¹, the conditions under which it may form and the various factors that can influence its reactivity do not seem to have been fully explored. For this reason its potential danger may often be overlooked.

A fuller account will be given elsewhere.

R. I. HUGHES
T. D. B. MORGAN
R. W. WILSON

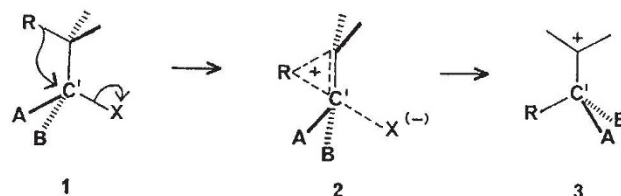
Shell Research Ltd,
Thornton Research Centre,
PO Box 1, Chester CH1 3SH, UK

Received February 4, 1974.

¹ Berzelius, J. J., *Lehrbuch der Chemie*, **2**, 367 (Dresden, 1826).

Stereochemistry of a carbonium ion rearrangement

CONCERTED rearrangements of the carbonium ion kind ($1 \rightarrow 3$) are usually supposed to go with stereochemical inversion at the migration terminus (C^2) and retention in the migrating group (R) (ref. 1). Many chemists have recorded one or other of these results but no one has shown both in one and the same acyclic molecule, largely because



it is very difficult to find a reaction in which both centres are chiral and both survive as chiral in the product. Rigid cyclic systems do show both results at once but this is not very informative as no other outcome is conceivable in a molecule which has no opportunity for internal rotation.

We have been studying² phosphinyl rearrangements (1 , $R = \text{Ph}_2\text{PO}$), attracted by the very high yields, usually more than 95%, of single products formed in these reactions. We wanted to look at the stereochemistry at the migrating phosphorus atom, since it does not follow automatically from the carbon case that retention will be the general rule and also at carbon (C^2 in 1) since we should like evidence on the detailed mechanism of the reaction: whether, for example, the two steps shown in (1) are concerted. This kind of question is worth asking because most accounts of carbonium ion rearrangements assume that electronegative groups like Ph_2PO will not migrate easily since they cannot support the positive charge in the transition state (2) .

In one of our reactions² ($4 \rightarrow 5$, $R^1 = R^2 = \text{Ph}$), a chiral migration terminus remained chiral in the product.

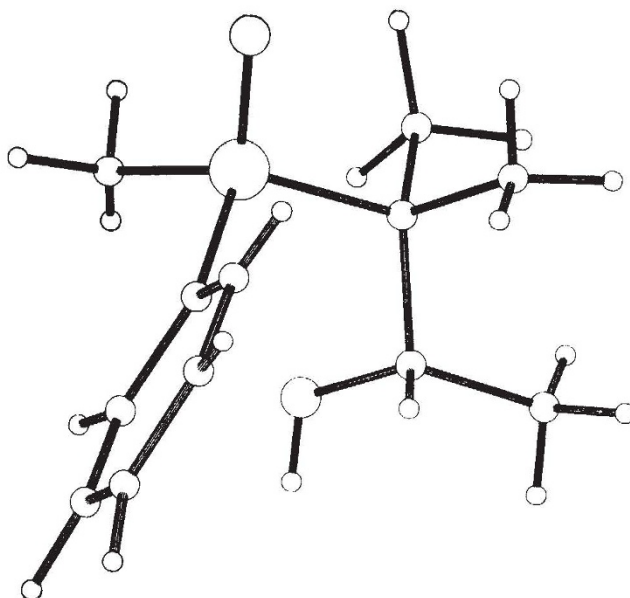


Fig. 1 Perspective drawing of the molecular structure of alcohol (7a).