

The catalytic activity measurements were made one month later by a flow method. The conversion ratio as a function of the reaction temperature is shown in Fig. 1. Scarcely any induced radioactivity was detected: nickel oxide system, 0.2 mr./hr. (γ -rays); aluminium oxide system, none; stannic oxide system, 0.4 mr./hr. (β -rays). On the assumption that the reaction is first-order, the apparent activation energy and the ratio of frequency factors before and after irradiation have been calculated and are shown in Table 1.

According to these results, the catalytic activity changes in every system: there is a small decrease with the nickel oxide system, an increase or decrease with the aluminium oxide system, and a remarkable increase with the stannic oxide system. Stannic oxide usually contains oxygen ion vacancies as an *n*-type semiconductor, and the number of these is readily increased by irradiation with alpha-particles which are produced by an (*n*, α) reaction with lithium-6 or boron-10 atoms. Nickel oxide contains excess oxygen ions as a *p*-type semiconductor and probably loses some of these on irradiation. The behaviour of the aluminium oxide system is probably due to its being an insulator.

The results of these experiments show that the larger the number of lattice defects, the more active is the semiconductor catalyst.

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¹ Taylor, E. H., and Wethington, J. A., *J. Amer. Chem. Soc.*, **76**, 971 (1954). Taylor, E. H., and Kohn, H. W., *ibid.*, **79**, 252 (1957). Clarke, R. W., and Gibson, E. J., *Nature*, **180**, 140 (1957). Hirota, K., Sakuyama, S., and Iizuka, G., *J. Chem. Soc. Japan* (Pure Chem. Section), **78**, 981 (1957).

² Weisz, P. B., and Swegler, E. W., *J. Chem. Phys.*, **23**, 1567 (1955).

A Simple Synthesis of Oxetanes

WE would like to report a simple method of synthesizing oxetanes. Oxetanes have generally been prepared by a multi-step procedure involving the basic elimination of a halide or acyl radical. The syntheses are involved, and yields are low to fair. Our method consists of dissolving a diol in a mineral acid, introducing the mixture into a heated solution of base, and distilling off the cyclic ether produced.

Using this method, we have prepared oxetane, 1-methyl oxetane and 2,2-dimethyl oxetane. Indications are that this synthetic method is generally applicable to the preparation of cyclic ethers, including oxiranes. Further work using this method is in progress.

Preparation of 2,2-dimethyl oxetane. 2 moles of sulphuric acid (111 ml., 96 per cent) were added to 2 moles of neopentyl glycol (208 gm.) and the mixture was stirred. The resulting solution was very viscous. A solution of 240 gm. sodium hydroxide in 107 ml. of water was brought to the boiling point in a 1-l., 3-neck flask equipped with a stirrer, dropping funnel and distilling head. The glycol solution was then added from the dropping funnel at such a rate as to maintain boiling. About 30 min. was required for this addition. Some heating of the dropping funnel with a burner was required to keep the viscosity of the glycol solution low enough for an

adequate rate of flow. 120 ml. of distillate was collected, which separated into two layers. The lower aqueous layer was separated and partially redistilled to recover the organic material. The organic layer from the partial redistillation was combined with the original organic layer and dried with calcium chloride. The dried organic layer was further dried with calcium hydride and distilled.

The product boiling between 79° and 83° C. amounted to 49.2 gm., or 29 per cent.

For further characterization, the product was again redistilled from calcium hydride. The fraction boiling between 79.2 and 80.3° C. (uncorrected) at a pressure of 756 mm. mercury was collected.

The density was found to be 0.8272 gm./ml. at 25° C. The refractive index, $N_D(25.1^\circ \text{C.})$ was 1.3956.

An infra-red spectrum was obtained, and found to be identical to one previously published¹, except that there was no indication of either carbonyl or hydroxyl in our sample.

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¹ Barrow and Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).

Cis-trans Isomerism of Thioindigo Dyes in the Solid State

As the result of some preliminary observations by Stearns¹, an extensive study was made by Wyman and Brode² of the absorption spectra of solutions of several thioindigo dyes in benzene and chloroform under various conditions of illumination. Evidence was obtained that in solution thioindigo and its derivatives exist in equilibrium as two forms (*cis* and *trans*), which give rise to separate absorption bands in the visible region. X-ray diffraction studies on crystalline thioindigo by Madame von Eller³ suggest, however, that in the solid state the dye is present in the *trans* form. It is thought that the electrostatic attraction between slight positive and negative charges on neighbouring sulphur and oxygen atoms, respectively, maintains the thioindigo molecule in the *trans* configuration and prevents isomerization⁴. Presumably in some cases these attractive forces will be weakened by solvents or by substitution in the thioindigo molecule.

Some observations have recently been made of the absorption spectra of several thioindigo compounds in the form of solid transparent films on quartz prepared by vacuum deposition. The results suggest that where substitution would not be expected to diminish the electrostatic charges on the sulphur and oxygen atoms the *trans* compound appears to be the stable form in the solid state; but where reduction of these charges would be expected a mixture of *cis* and *trans* forms is found. Thus, as is seen in Fig. 1, solid films of thioindigo and 6:6' dichlorothioindigo both exhibit a sharp absorption band in the visible region indicative of the sole presence of the *trans* isomer in the solid state. The presence of chlorine atoms in the 6 and 6' positions in the thioindigo molecule should increase the negative character of the oxygen atom, and thus enhance the stability of the *trans* form. The introduction of methyl groups into the 4 and 4' positions of this derivative of thio-