

and ordered spinel structures respectively. This is in accordance with the conclusions arrived at during the investigation⁵ of ZnO-Cr₂O₃ system by DTA and of ZnO-Al₂O₃ system by X-ray analysis.⁶ The spinel formation, in the present case, may be due to the reaction:



and the exothermic region of the thermogram could be indicative of the crystallisation of the oxides together with the spinel formation. The co-precipitated catalyst, heated to 500° C. (S.A. 148 m²/g.) when no spinel is formed, was investigated for the decomposition of isopropyl alcohol. Experiments were conducted in the temperature region of 335° to 410° C. employing different contact times. The extent of dehydrogenation and dehydration occurring simultaneously was evaluated by gas-chromatographic analysis of the products, namely, acetone, water and undecomposed alcohol. The initial slopes of the concentration-time curves were used in the Arrhenius plots which gave the values of 11 kcal/mole and 6.4 kcal/mole as the activation energies for the dehydrogenation and dehydration reactions respectively. These values agree well with the values for dehydrogenation on pure ZnO and dehydration on pure alumina.⁷ The results would therefore indicate that the system heated to 500° C. behaves like a physical mixture of the two constituent oxides.

Decomposition studies on the system heated to 840° C. (S.A. 46 m²/g.) ensuring complete spinel formation, showed decreased dehydrogenation activity while the dehydration remained apparently unaltered. However, the surface area had decreased to one-third the value obtained for the system heated to 500° C. This could be ascribed to the destruction of the fine pore structure on heating as has been borne out by an actual pore-size distribution analysis in the present instance. The results also indicate that the dehydration activity of the system has considerably increased on the basis of unit area of the catalyst. This observation is in contradiction to that of Schwab,⁸ whose extensive investigations show that heat treatment of oxides reduces dehydration activity while in many cases enhancing dehydrogenation. Branson,⁶ based on X-ray diffraction and inert marker studies, has conclusively proved the one way diffusion of zinc oxide into aluminium oxide resulting in a solid solution followed by the formation of spinel. In the present instance also, the results would indicate the formation of a spinel structure as formulated by Bran-

son, namely, the formation of a zinc oxide core surrounded by alumina. Such a structure would predominantly expose alumina on the surface, effectively concealing most of ZnO, thus resulting in increased dehydration activity accompanied by loss of dehydrogenation.

X-ray diffraction studies of the mixed oxide heated to 500° C. showed only four broad ill-defined lines which could be due to the non-crystallinity of the material and the presence of lattice heterogeneity while that obtained with the sample, heated to 840° C., agreed fairly with that obtained for heated γ -Alumina thus lending support to the type of spinel structure postulated above.

In conclusion, catalytic activity studies might be useful in the elucidation of the mode of solid state reactions and structural changes occurring in mixed oxide systems.

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Dept. of Chemistry, B. VISWANATHAN.
Indian Inst. of Technology, V. SRINIVASAN.
Madras-36, October 16, 1969. M. V. C. SASTRI.

1. Eucken, A. and Heuer, K., *Z. Physik. Chem.*, 1950, **196**, 49.
2. Otwinowska, H., Treszczanowicz, E. and Ciborowski, S., *Actes 2eme Congr. Inter. de catalyse*, 1961, **2**, 1733.
3. Sharf, V. Z., Freidlin, L. Kh., German, E. N., Samokhvalov, G. I. and Papko, T. S., *Kinetics and Catalysis*, 1968, **9**, 784.
4. Upreti, M. C., Kuricose, J. C. and Sastri, M. V. C., *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, 1963, **11**, 651.
5. Bhattacharya, S. K. and Ramachandran, V. S., *Proc. Natl. Inst. Sci.*, 1959, **12**, 23.
6. Branson, D. L., *J. Am. Ceram. Soc.*, 1965, **48**, 591.
7. Unpublished results from this laboratory.
8. Schwab G. M. and Schwab-Agallides, E., *J. Am. Chem. Soc.*, 1949, **71**, 1809.

CHEMICAL INVESTIGATION OF RHODODENDRON PONTICUM HOOK.

PLANTS belonging to the genus *Rhododendron* (fam.: Ericaceae) are known to possess medicinal and poisonous properties.¹ The oils obtained from the flowers and leaves of *Azalea pontica* (*R. ponticum*) were recorded to be highly toxic and to possess bacteriostatic activity. The plant was shown to contain arbutin and andromedotoxin, especially in flowers and in lesser amounts in stems, leaves and roots.² The results obtained from a systematic chemical investigation of the leaves of this plant are described here.

The powdered leaf was successively extracted with light petrol (b.p. 60–80°), chloroform and methanol. The petrol extract, on concentration to a low volume, gave a solid (fraction 1). The mother liquor was evaporated to a residue which was saponified. The unsaponifiable matter was treated with acetone when crystals deposited (fraction 2). Further concentration of the acetone mother liquor yielded crystals (fraction 3). Fractions 1 to 3 were united and chromatographed over neutral alumina. The residue from the petrol eluate, on crystallisation from benzene-petrol, yielded substance A recorded below. The mother liquor was evaporated and the residue was crystallised from acetone yielding colourless nodules, m.p. 74–76°. The substance did not answer the usual triterpenoid colour reactions and did not form an acetate. The petrol-benzene (9 : 1, 4 : 1, 1 : 1) eluates furnished a crystalline solid which was identified as friedelin³ (substance A): colourless needles from benzene-petrol, m.p. 250–52°, $[\alpha]_D = -30.5^\circ$; 2 : 4-dinitrophenylhydrazone, m.p. 298–300°. The identity was confirmed from mixed m.p. and superimposable I.R. spectra. The benzene-chloroform (49 : 1, 19 : 1, 9 : 1, 4 : 1, 1 : 1) and chloroform eluates yielded epifriedelanol³ (substance B): colourless plates from chloroform-alcohol, m.p. 281–82°, $[\alpha]_D = +25.1^\circ$; benzoate, m.p. 250–52°, $[\alpha]_D = +28.2^\circ$. Confirmation of the identity was obtained from mixed m.p.s., superimposable I.R. spectra and identical colour reactions.

The chloroform extract was concentrated, diluted with ether and the resulting solution was shaken with 5% sodium hydroxide when a precipitate separated at the interphase. This was filtered, dissolved in alcohol and decomposed with acid. Dilution and removal of the alcohol under reduced pressure gave a solid which crystallised as colourless needles from absolute alcohol (substance C): m.p. 279–82°, $[\alpha]_D = +59.0^\circ$ (pyridine); acetate, m.p. 281–82°, $[\alpha]_D = +72.3^\circ$; methylester, m.p. 110–12°, $[\alpha]_D = +53.3^\circ$; acetate of methylester, m.p. 243–46°, $[\alpha]_D = +68.0^\circ$. These properties indicated its identity with ursolic acid³ and the identity was confirmed from mixed m.p.s. The precipitate, obtained on neutralization of the alkali extract above, was treated with diazomethane and the residue was chromatographed over neutral alumina when methyl ursolate was obtained. The result was confirmed by preparation of acetylmethylursolate. The alkali-insoluble fraction was saponified

and the unsaponifiable matter was treated with acetone yielding a solid deposit. This was chromatographed over neutral alumina. The petrol-benzene (19 : 1, 9 : 1, 4 : 1) eluates gave friedelin. The benzene-chloroform (49 : 1) eluate gave a substance, m.p. 176–77° (colourless plates from petrol, substance D); Liebermann-Burchard reaction: pink-violet-blue-green. The benzene-chloroform (19 : 1, 9 : 1, 4 : 1, 1 : 1) and chloroform eluates yielded a substance, m.p. 215–16° (colourless nodules from benzene-petrol, substance E); Liebermann-Burchard reaction: pink. As the yields were poor, substances D and E were not studied further.

The methanol extract was concentrated under reduced pressure to a low volume, hydrolysed with 7% sulphuric acid and extracted with ether. The residue from the ether extract, on crystallisation from dilute alcohol, gave quercetin, m.p. 302–06° (substance F). This gave identical U.V. spectrum as authentic quercetin³; penta-acetate, m.p. 195–97° (mixed m.p. undepressed).

All rotations were taken in chloroform except where otherwise stated.

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1. Chopra, R. N., Badhwar, R. L. and Ghosh, S., *Poisonous Plants of India*, Manager of Publications, Delhi, 1949, 1, 613.
2. Korta, J., *Chem. Abs.*, 1954, 48, 5445.
3. Rargaswami, S. and Sambamurthy, K., *Proc. Ind. Acad. Sci.*, 1961, 54 A, 99.

IN-VITRO SENSITIVITY OF VIBRIO CHOLERAЕ BIOTYPE ELTOR TO CLIOQUINOL (ENTEROVIOFORM)

TETRACYCLINE has been proved to be valuable for the treatment of cholera¹⁻³ and for chemoprophylaxis of household contacts of cholera patients.⁴ However, the high cost of the drug restricts its routine use in cholera-affected countries. Efforts have been made during the recent years to find out a cheaper substitute for the same. A laboratory evaluation of clioquinol (vioform) as a prophylactic agent against cholera has been reported.⁵ The results of the study showed that *Vibrio cholerae* and its biotype *Eltor* were inhibited by a relatively low concentration of the drug. It was suggested