## DETERMINATION OF MISCIBILITY CHARACTERISTICS OF HIGHLY REACTIVE LIQUIDS

*Sir:*

A method has been devised in our Laboratory for determining the miscibility characteristics of highly reactive liquids. The need for such information arose when inconsistent results obtained from experiments on the kinetics of the pentaborane–9-hydrazine reaction could only be explained by the fact that these two compounds are immiscible. The rapid rate of reaction between the two suggested that the opposite was true. Since the pentaborane-9 and hydrazine react too rapidly at room temperature for observation by eye, high-speed motion pictures were taken of the phenomena occurring when a drop of hydrazine was added to a bulk quantity of pentaborane-9. By this means it was established definitely that despite rapid reaction at the interface between the two liquids, the bulk liquids are immiscible.

A drawing of the apparatus used for these studies is shown in Fig. 1. The hydrazine was contained in the upper tube (C). The breaker (B) was held in position with an electromagnet (A). When the current to the electromagnet was turned off, the breaker fell and released the hydrazine (D), which then traveled down the tube and flowed dropwise from the drip tip (E) into the pentaborane (F). Earlier experiments had shown that this slower method of addition was required to prevent the splashing and turbulence caused by dropping hydrazine directly from its container into the pentaborane. Since hydrazine is more dense than pentaborane-9 (1.0 g./cc. *vs.* 0.6 g./cc.), the drop penetrated through the bulk liquid after contact.

To facilitate observation, a trace of yellow dye was added to the hydrazine, and the progress of the drop as it descended through the colorless pentaborane was recorded on color film. The apparatus was lighted from the rear by a collimated beam of light. In initial experiments the edges of the pentaborane-9 (F) were opaque, probably due to reflectance of the light by the curved cylindrical glass; consequently the field of view was grossly restricted. To prevent this condition the tube was surrounded in later experiments by a beaker of carbon tetrachloride. The indices of refraction of carbon tetrachloride and Pyrex are essentially the same; thus, no distortion of light occurred at the glass–liquid interface and the column of pentaborane-9 was in clear view.

Photographs were taken at speeds of 1100 to 1500 frames per second. Comparison films were taken of the addition of water to pentaborane (also an immiscible system) and of water to a pentaborane-9–dioxane solution (miscible system by virtue of the common solvent, dioxane). When ether water or hydrazine was added to pentaborane-9, the drops travelled essentially intact to the bottom of the tube, the dye remaining with the descending drop. The only difference between these two chemical systems was in the chemical reactivity, as evidenced by more rapid gas bubble formation (hydrogen) at the droplet liquid interface in the case of hydrazine and pentaborane-9.

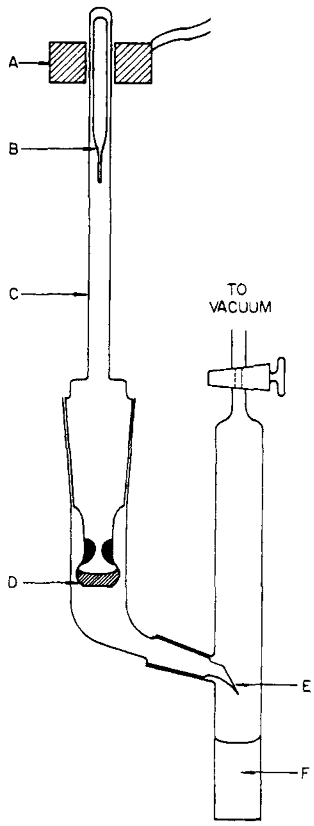

Fig. 1.—Apparatus for miscibility study.

A considerably different situation was observed when water was added to the pentaborane-9–dioxane solution. In this case the drops of water broke up immediately on contact with the pentaborane-9, vapor bubbles emanated from throughout the solution, and the entire system took on the color of the dye.

The authors recommend this technique for the determination of miscibility characteristics in other systems involving highly reactive liquids.

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## DEMERCURATION ROUTE TO THE NORBORNYL CATION[1,2]

*Sir:*

Heterolysis of carbon–metal bonds in the sense of formula I is interesting and important in olefin oxidations by mercury,[3] lead,[4] and thallium[4,5] salts. With 1,2-diphenyl-2-methoxyethylmercuric

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(3) *E.g.*, (a) D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **33**, 1002 (1955); (b) A. C. Cope, N. A. Nelson and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954); (c) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 238 (1951).

(4) R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

(5) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).