into the pressurized reactor by hypodermic syringes and the pressure was maintained at 30 p.s.i. with no monomer vented. Copolymer propylene contents were measured by infrared absorption at 7.25 *u*.

Propylene is less reactive than ethylene with all the catalysts employed and it accumulates in the reactor causing a linear increase in the average propylene content of the gross copolymer with increasing yield of copolymer (Fig. 1). Ethylene and propylene show distinctly different relative reactivities with catalysts prepared from a common reducing agent, $Al(i\text{-}Bu)_3$, and different transition metal compounds. Propylene relative reactivity increases in the series $HfCl_4 < ZrCl_4 < TiCl_4 < VOCl_3 < VCl_4$. This increase appears to correspond to increasing electronegativity of the transition metal center. However, there is no significant difference in the relative reactivity of the two monomers when the reducing agent is changed from $Al(i\text{-}Bu)_3$, to $Zn(C_6H_5)_2$, $Zn(n\text{-}Bu)_2$, or CH_3TiCl_3,[6] using a common transition metal compound, VCl_4. These reducing agents differ widely in general steric configuration and in bond hybridization, electronegativity, valence, and size of the metal ion. The common denominator in this series is the reduction of VCl_4 wholly, or partially, to the divalent state.[3,5] Significantly, the two transition metal compounds ($CH_3TiCl_3 + VCl_4$), form a highly active catalyst and the dependence of copolymer composition on polymer yield is that for VCl_4 catalysts rather than for the $Al(i\text{-}Bu)_3$–$TiCl_4$ catalyst.[7]

Selection between two monomers at the growing chain end is a sensitive measure of the structure and polarity of the active propagation site, and a change in this selectivity implies a change in the *nature* of the active site. The fact that the relative monomer reactivities are altered by changes in the transition metal center but not by changes in the reducing agent implies that propagation occurs at the transition metal center, with no direct participation by the reducing agent.[3] This further suggests that the formation of bimetallic complexes involving the metal of the reducing agent is not an essential feature of the catalytic function.

Natta and co-workers also have observed differences in comonomer reactivity ratios using catalysts composed of aluminum trihexyl and certain transition metal halides,[8] but they did not vary the reducing agent. The available data do not allow a rigorous comparison of the present data with the published results; however, a qualitative comparison indicates that the propylene content of the initial copolymer in their case is higher than the values reported here for the three transition metal compounds common to both studies ($TiCl_4$, $VOCl_3$, VCl_4) by a factor of 0.1-0.5. No specific significance is attached to the fact that the two sets of data are not identical since the experiments were carried out with different reaction diluents, pressures, temperatures, degree of monomer dispersion, and possibly different degrees of reduction of the transition metal. It is significant that the trend is the same in both cases. The published opinion of Natta and co-workers[1,8] favors propagation from an aluminum center in a bimetallic complex, although their copolymerization data are more consistent with our view above[3].

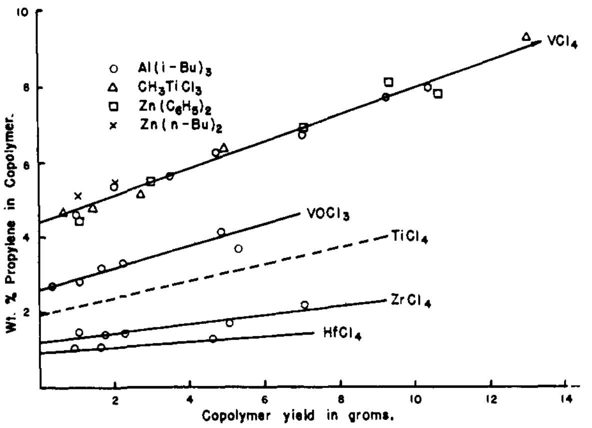

Fig. 1.—Effect of catalyst structure on copolymer composition: in all experiments the monomer feed contained 28% propylene, 69% ethylene and $\simeq 3\%$ ethane (area per cent. by vapor chromatography).

RESEARCH DEPARTMENT WAYNE L. CARRICK
UNION CARBIDE PLASTICS COMPANY FREDERICK J. KAROL
DIVISION OF UNION CARBIDE CORP. GEORGE L. KARAPINKA
BOUND BROOK, NEW JERSEY JOSEPH J. SMITH

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[5] W. L. Carrick, A. G. Chasar and J. J. Smith, Paper No. 4, Polymer Division, 134th Meeting of the American Chemical Society, Chicago, Illinois, September 7-12, 1958.

[6] Belgian Patent 553,447.

[7] Experimental points are not given for the AlR_3–$TiCl_4$ case since more than one active species is present and reproducibility is poor.

[8] G. Natta, *J. Polymer Sci.*, **34**, 21-48, 88-92 (1959).

STRONGLY BASIC SOLUTIONS IN TETRAMETHYLENE SULFONE (SULFOLANE)

Sir:

The small autoprotolysis constant and moderately good ionizing characteristics of sulfolane suggest it as a solvent in which one could study a very wide range of acidities.[1] Using solutions of phenyltrimethylammonium hydroxide in aqueous sulfolane, we have been able to measure pK_a's of neutral proton acids distinctly weaker than any previously evaluated by the Hammett method.[2] Table I presents these values along with those of other weak acids obtained by similar methods in aqueous hydrazine[3] and aqueous ethylenediamine.[4]

$H_- = 20$, our most basic value of the H_- function[2] (Fig. 1), is about 4 units more basic than any proper H_- previously evaluated.[3,4] The 0.01 M solution of base in sulfolane containing 5 mole % water is over 10^6 times more basic than the corresponding aqueous solution, *i.e.*, H^- is over 6 units greater. The contribution to this exalted basicity resulting from the reduction of water activity

$$HA + OH^- \rightleftarrows A^- + H_2O$$

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[1] R. L. Burwell, Jr., and C. H. Langford, THIS JOURNAL, **81**, 3799 (1959).

[2] M. A. Paul and F. A. Long, *Chem. Reviews*, **57**, 1 (1957).

[3] N. C. Deno, THIS JOURNAL, **74**, 2039 (1952).

[4] R. Schaal, *J. Chim. Phys.*, **52**, 784, 796 (1955). We believe that certain details of Schaal's procedures subject his values to substantial error.

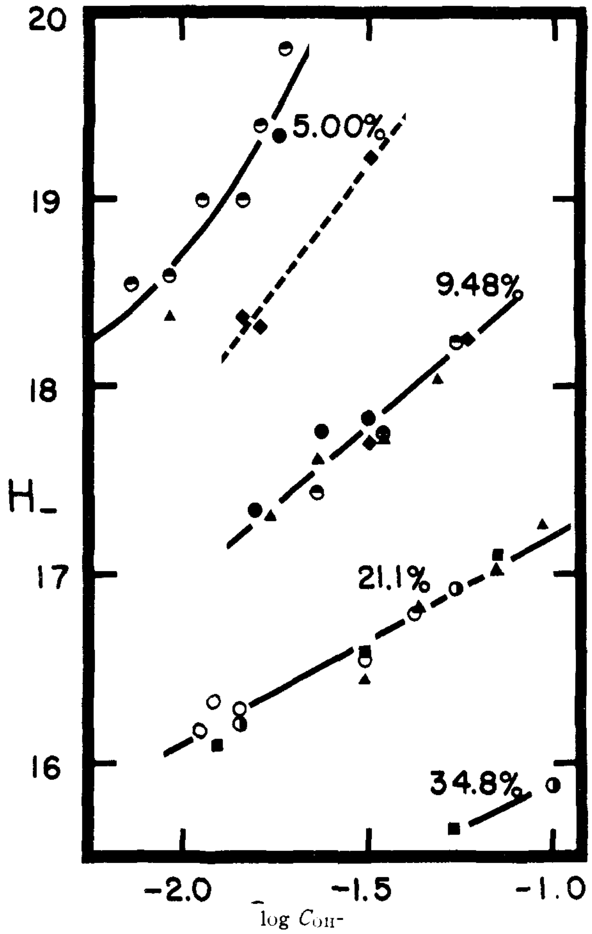

Fig. 1.—H_ function.

was estimated from vapor pressure measurements on sulfolane–water solutions to be about a factor of about 10. Very probably, the remaining factor of 10^5 enters largely *via* the activity coefficient of the hydroxide ion. Alkali metal hydroxides are insoluble in sulfolane and one can get hydroxide ion into solution only by using a large, polarizable cation. Analogous factors seem responsible for the high basicity of potassium *t*-butoxide in dimethyl sulfoxide,[5] a solvent similar to sulfolane in many ways.

TABLE I

ACIDITY CONSTANTS OF WEAK ACIDS

Indicator acid[d]	This research[a]	Aqueous hydrazine[3]	Aqueous ethylenediamine[4]
p-Nitrobenzyl cyanide[c]	(13.45)[b]	13.43	13.45
6-Bromo-2,4-dinitroaniline	13.71		
3-Nitrocarbazole		14.16	15.10
○ 2,4-Dinitroaniline	15.34		15.80
■ 4-Nitrodiphenylamine	15.76	15.43	
◑ 4,4'-Dinitrodiphenylmethane[c]	15.82	15.90	
▲ 4-Chloro-2-nitroaniline	17.21		
◆ 2-Nitrofluorene[c]	17.59		
⊖ *p*-Nitroaniline	18.47		
● 9-Phenylfluorene[c]	18.49		

[a] Estimated precision in pK_a is about 0.1 [b] Assumed. [c] Because of the rapid oxidation of the conjugate base, measurements required complete exclusion of oxygen. [d] Symbols at left refer to Fig. 1.

Similarly, a 0.01 M solution of sulfuric acid in sulfolane is much more acidic than the corresponding aqueous solution.

With 21 and 35 mole % water (Fig. 1), plots of H_- *vs.* log C_{OH^-} are linear with unit slope. However, the slope steadily increases as water content is lowered, apparently because of strong solvation of hydroxide ion by water molecules. If each hydroxide ion removes four water molecules, the slopes are reasonable. In agreement with this, at concentrations of hydroxide ion lower than shown in Fig. 1, the slope decreases considerably in the 5 mole % solution.

The anomalous behavior of 2-nitrofluorene in the 5 mole % solution may have one of two origins: One may no longer have a good H_- function at the lowest water concentration, or 2-nitrofluorene may not be a simple proton acid. The observed color change may result from addition of OH^- to the fluorene ring as, indeed, must happen with *m* dinitrobenzene for which one may measure an apparent pK_a of 16.8.[4]

(5) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, THIS JOURNAL, **81**, 5774 (1959).

(6) Monsanto Fellow, 1957–1958. National Science Foundation Pre-Doctoral Fellow, 1958–1959.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
COOPER H. LANGFORD[6]
ROBERT L. BURWELL, JR.

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ISOMERIZATION OF ORGANOBORANES DERIVED FROM BRANCHED-CHAIN AND RING OLEFINS—FURTHER EVIDENCE FOR THE ELIMINATION-ADDITION MECHANISM OF ISOMERIZATION

Sir:

The isomerization of organoboranes[1] occurs with remarkable ease under hydroboration conditions.[2] This facile shift of the boron atom down the *n*-alkane chain, from an internal position to the terminal position, makes possible the simple conversion of internal olefins into *n*-alkyl derivatives. In order to determine the full scope of this reaction, it was important to establish whether the boron atom can be shifted past an alkyl branch, or from a naphthene ring into a side-chain.

Hydroboration of 2,4,4-trimethyl-2-pentene at 25°, then oxidation with alkaline hydrogen peroxide, gives 99% 2,4,4-trimethyl-3-pentanol, with only 1% of the tertiary alcohol, 2,4,4-trimethyl-2-pentanol (vapor phase chromatography analysis). However, if the initial hydroboration product is heated for one hour at 160° (refluxing diglyme), the reaction product is essentially pure 2,4,4-trimethyl-1-pentanol. Similarly, 4,4-dimethyl-2-pentene yields 57% of 4,4-dimethyl-2-pentanol and 43% of 4,4-dimethyl-3-pentanol. After the isomerization treatment, the product is 96% 4,4-dimethyl-1-pentanol.

(1) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, THIS JOURNAL, **79**, 5190 (1957).

(2) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6434 (1959).