# COMMUNICATIONS TO THE EDITOR

## THE SOLUBILITY OF HYDROGEN CHLORIDE AT LOW TEMPERATURES—A MEASURE OF THE BASIC PROPERTIES OF AROMATIC NUCLEI

*Sir:*

There is now considerable evidence that aromatic nuclei possess basic properties. Klatt[1] observed that aromatic compounds dissolve in liquid hydrogen fluoride, whereas saturated hydrocarbons do not. Winstein and Lucas[2] and, more recently, Keefer and Andrews[3] attribute complex formation between silver ion and aromatic hydrocarbons to the basic properties of the aromatic nuclei. Fairbrother[4] correlated changes in the apparent dipole moments of iodine in several hydrocarbon solvents with changes in the probable donor character of the $\pi$ electrons in the hydrocarbon. Finally, the absorption spectra of solutions of iodine in aromatic hydrocarbons show changes which can also be correlated with the basic properties of the solvent.[5]

In the course of studies of the action of the catalyst couple, aluminum chloride–hydrogen chloride, on aromatic hydrocarbons at low temperatures, we have observed that the solubility of hydrogen chloride varies considerably with different aromatic hydrocarbons. The variation in solubility cannot be correlated with any of the usual physical properties of the solvent, but it can be correlated with the predicted variation in the basic properties of the compounds.

In order to investigate this phenomenon more carefully, we developed a method for measuring Henry's law constant with a precision of approximately 1 part in 500. Toluene is used as solvent. A solution of 10 moles of toluene and 1 mole of aromatic hydrocarbon is prepared. The solution is maintained at $-78.51°$ and small quantities of hydrogen chloride are introduced. Henry's law is followed over a wide range of concentration. From the observed pressures, the constant is calculated from the usual expression, $p = kx$, where $p$ is the pressure of hydrogen chloride, $x$ is its mole fraction and $k$ is the desired constant.

The following values for $k$ (in mm.) have been obtained: (1) trifluoromethylbenzene, 332; (2) chlorobenzene, 318; (3) benzene, 308; (4) toluene, 299; (5) *p*-xylene, 294; (6) *o*-xylene, 286; (7) *m*-xylene, 278; (8) pseudocumene, 272; (9) hemimellitene, 265; (10) mesitylene, 254.

It is apparent that the order of increasing solubility is identical with the order of increasing reactivity toward the usual electrophilic substituting agents. Therefore, Henry's law constant may be taken as a measure of the relative basicity of the ring. It is particularly interesting that the method is sufficiently sensitive to differentiate between the isomeric xylenes and trimethylbenzenes.

We are now applying the procedure to other benzenoid derivatives, polynuclear hydrocarbons, heterocyclics and olefins. The data should be useful in giving a quantitative measure of the effect of structure on the relative basicities of these compounds.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
JAMES BRADY

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(1) Klatt, *Z. anorg. allgem. Chem.*, **234**, 189 (1937); Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 293–294.

(2) Winstein and Lucas, THIS JOURNAL, **60**, 836 (1938).

(3) Abstracts of Papers Presented to the Division of Organic Chemistry at the 115th Meeting of the American Chemical Society, San Francisco, 1949, p. 47.

(4) Fairbrother, *J. Chem. Soc.*, 1051 (1948).

(5) Benesi and Hildebrand, THIS JOURNAL, **70**, 2832 (1948); **71**, 2703 (1949).

## PROPARGYLGLYCINE: AN ACETYLENIC AMINO ACID ANTAGONIST[1,2]

*Sir:*

As part of a research program designed to get information concerning the basis for the preparation of specific metabolite antagonists, we prepared and studied the vinylene-type unsaturated amino acids, allylglycine, methallylglycine, crotylglycine and 2-amino-5-heptenoic acid.[3] Since allylglycine was a potent inhibitor of the growth of bacteria and yeast, we deemed it desirable to prepare the corresponding acetylenic amino acid, propargylglycine. In this communication we wish to report the synthesis and preliminary microbial-growth inhibitory properties of propargylglycine.

**Diethyl Propargylformamidomalonate.**—To a solution containing 0.92 g. (0.04 g. atom) of sodium dissolved in 75 ml. of absolute alcohol was added 8.12 g. (0.04 mole) of diethyl formamidomalonate.[4] Five grams (0.042 mole) of propargyl bromide[5] in 20 ml. of ethanol was added and refluxed for eighteen hours. After concentration to dryness, the residue was taken up in a mixture of chloroform and water. The residue from the chloroform was recrystallized from water. The diethyl propargylformamidomalonate melted at 69–70°, and the yield was 90%. An analytical sample was obtained from di-*n*-butyl ether, m. p. 71–72°.

*Anal.* Calcd. for $C_{11}H_{15}NO_5$: C, 54.77; H, 6.22; N, 5.81. Found: C, 54.85; H, 6.34; N, 5.59.

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(2) The authors gratefully acknowledge the technical assistance of Mrs. Ann E. Johnson and Mr. Robert P. Martin.

(3) (a) Dittmer, Goering, Goodman and Cristol, THIS JOURNAL, **70**, 2499 (1948); (b) Goering, Cristol and Dittmer, *ibid.*, **70**, 3310, 3314 (1948).

(4) A. Galat, *ibid.*, **69**, 965 (1947).

(5) A. Kirrmann, *Bull. soc. chim.*, IV, **39**, 698 (1926).