polar. Its reactions with bromine, iodine bromide and iodine chloride were studied, using carbon tetrachloride and acetic acid as solvents. In this way, polarity effects were brought out clearly.

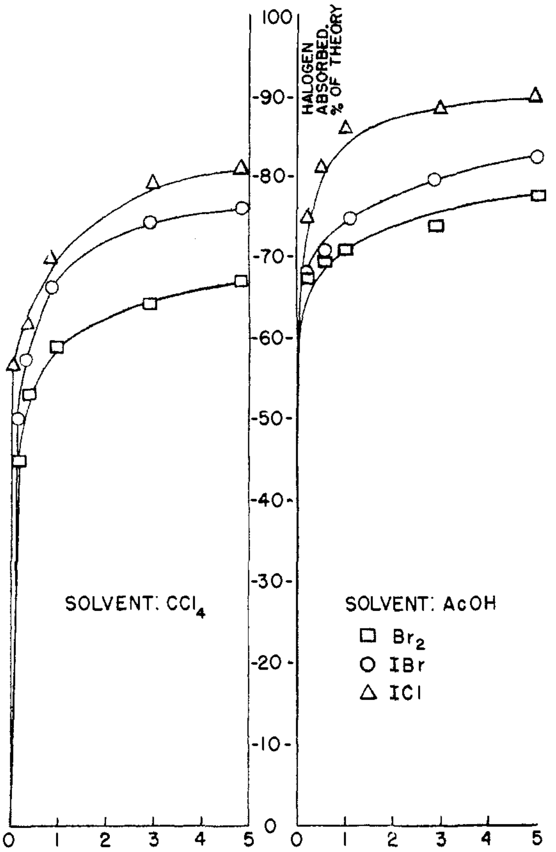

Fig. 1.

Representative results are shown in Figs. 1 and 2. They are in agreement with the accepted polar mechanism of olefin addition reactions,[1] since the most polar halogen (iodine monochloride) adds fastest, the least polar (bromine) slowest, and the more polar solvent (acetic acid) accelerates the addition. It is remarkable that bromine is consumed far beyond the theoretical limit of addition; in carbon tetrachloride in two days 137%, and in three days 152% of the theoretical amount of bromine had disappeared. In acetic acid the bromine absorption was 106% after three days and 118% after five days. No evidence of substitution was found with either of the mixed halogens in any solvent. This seems to indicate that the polarity of an inter-halogen molecule inhibits its break-up into atoms as required for substitution.[2] The inference is that bromine is also somewhat polarized in acetic acid solution.

Solutions of iodine monobromide, which are no more difficult to prepare than those of bromine, might well replace the latter, now generally used, for quantitative unsaturation tests. With iodine monobromide decoloration occurs much more rapidly and substitution is absent.

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(2) H. C. Brown, M. S. Kharasch and T. H. Chao, THIS JOURNAL, **62**, 3435 (1940).

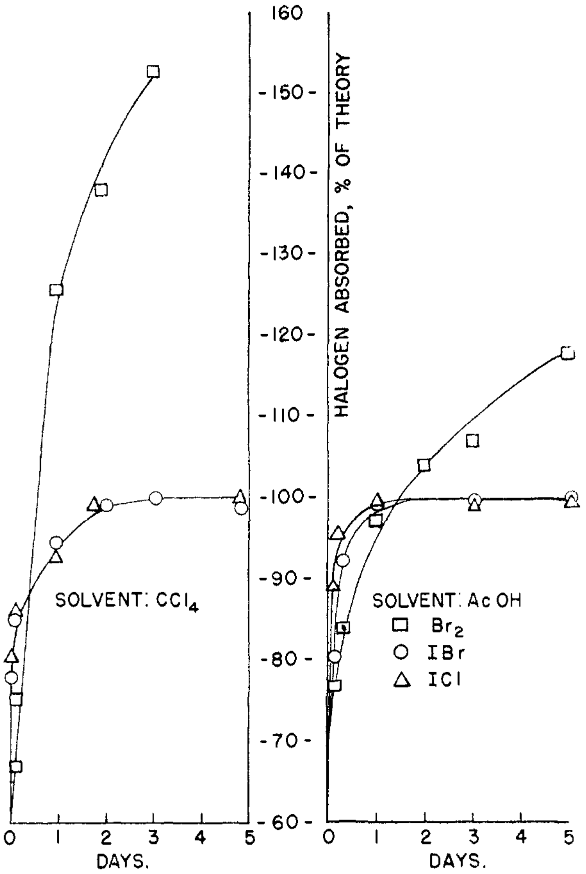

Fig. 2.

Experimental

Ten mg. of cyclohexene was mixed with 5 ml. of $0.05N$ halogen solution and kept in the dark at 25° for periods ranging from 15 seconds to five days. Then the mixture was stirred mechanically into excess aqueous iodide solution and the liberated iodine titrated. With acetic acid as the solvent, the iodide solution was also buffered with disodium phosphate, for the dihalocyclohexanes are easily dehalogenated by iodide ion at low *p*H. From the results of the titration the halogen absorbed by the cyclohexene was calculated.

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The Application of the Glass Electrode in Liquid Ammonia Systems[1,2]

BY ARNO H. A. HEYN AND MARTHA J. BERGIN

RECEIVED MARCH 24, 1953

Glass electrodes have been used for measurement of the hydrogen ion activity in some cases in nonaqueous solutions.[3,4] However, a glass electrode which had been thoroughly hydrated by immersion in water was used. It is likely, therefore, that the system measured was "non-aqueous" only with respect to the solution before the electrode had been immersed and that equilibria with the hydrated glass surface established the potentials. Work by

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(1) From a Ph.D. Thesis of Martha J. Bergin, May, 1952.

(2) Supported in part by a Grant-in-aid of the Research Corporation, New York, N. Y.

(3) L. Lykken, *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **16**, 219 (1944).

(4) L. Lykken, ASTM *Symposium on pH Measurement*, Technical Publication No. 73, p. 71 (1946).

Hubbard and co-workers[5] has shown that the glasses which were more soluble in water, and were therefore more highly hydrated, showed the best *p*H response when used as electrodes. This points out the importance of hydration for glass electrode action.

The question arises, whether glass electrode action exists in liquid ammonia solution. Liquid ammonia ionizes to a very slight extent to form NH_4^+ and NH_2^-, where the ammonium ion, analogous to the hydronium ion, is the solvated proton.[6,7] This suggests that glass electrodes might respond to changes in the ammonium ion activity in liquid ammonia in a similar manner as to changes in the hydronium ion concentration in aqueous solutions.

The following conditions would have to prevail in order to make glass electrode action in liquid ammonia possible: 1. The measuring instrument used must be sufficiently sensitive so that the increase in the resistance of the glass electrode with a decrease in temperature to below the boiling point of ammonia does not interfere. 2. Suitable reference electrodes for liquid ammonia solutions must be used. 3. The glass used must be solvated by liquid ammonia. 4. The ammonium ions in the glass must be in equilibrium with those in the solution.

After initial experiments failed to give evidence for electrode action in liquid ammonia a systematic investigation of points 1, 2, and 3 showed that the failure of glass electrode action is not due to these causes, but is probably due to lack of an equilibrium of the ammonium ion between the glass and the solution.

In order to show that the decrease in temperature necessitated by the low boiling point of ammonia (−33.4°) was not responsible for lack of glass electrode action, the electrical resistance of glass electrodes was measured over the range 6 to 50° in aqueous solutions and over −35 to 45° in alcohol–water solutions. In both cases the resistance was found to follow the relationship known to hold for higher temperatures[8]

$$\log R = A + (B/T)$$

where *R* is the observed resistance, *T* the absolute temperature and *A* and *B* are constants (Fig. 1). In addition, *p*H measurements could be obtained both at room temperature and at −29° in the water–alcohol system. In liquid ammonia solutions, however, the resistance of the glass electrodes appeared to be infinite (no current could be measured) at −35° or even when the temperature was increased to −1°.

Lead–lead nitrate electrodes were used as reference electrodes in the cell system studied

Lead	$Pb(NO_3)_2$, 0.1 *M*	NH_4NO_3 Varying concn.	Glass membrane	NH_4NO_3, 0.1 *M*	$Pb(NO_3)_2$ 0.1 *M*	Lead
	Liquid ammonia			Liquid ammonia		

The potential of a reference electrode in such a system is unimportant provided it remains constant. Although the lead–lead nitrate electrode is not useful in aqueous work since a reproducible potential cannot be obtained owing to lead hydroxide formation, this electrode has been used in electrochemical measurements in liquid ammonia. In many respects, its significance for electrochemical measurements in liquid ammonia parallels that of the hydrogen electrode in aqueous solutions.[9] Solvation of the glass by ammonia is expected to have a bearing on glass electrode action in liquid ammonia. For all measurements in liquid ammonia solutions the glass electrodes used were left in contact with the liquid ammonia solution for several hours, and in some cases for days. Under these conditions solvation should have occurred. To be perfectly sure, however, that ammonium ions had entered the glass structure, sodium ions were partially replaced by ammonium ions electrolytically by the method of Hurd and co-workers.[10,11] According to nitrogen analyses of the glass, 60% of the sodium ions were thus replaced. Such membranes gave equally negative results.

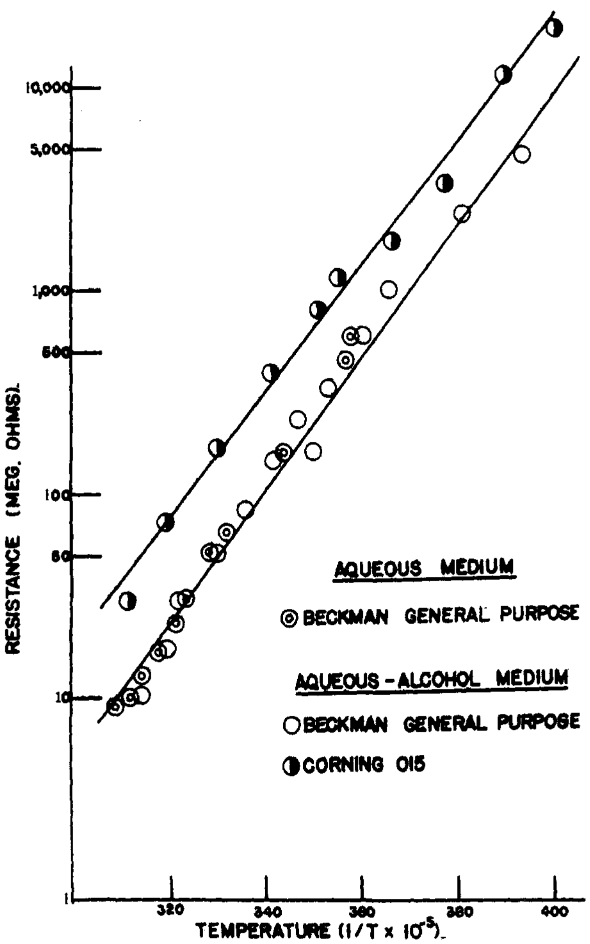

Fig. 1.—Resistance of glass electrodes *vs.* temperature.

All of the several glasses tried (Corning 015, Beckman "General Purpose," Beckman "Type E") failed to show glass electrode response in liquid ammonia solution.

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(5) D. Hubbard, *J. Research Natl. Bur. Standards*, **36**, 511 (1946).

(6) V. A. Pleskov and A. M. Monoszon, *Acta Physiochim. U.S.S.R.*, **1**, 725 (1935).

(7) E. C. Franklin, This Journal, **27**, 820 (1905).

(8) E. L. Eckfeldt and G. A. Perley, *J. Electrochem. Soc.*, [2] **98**, 37 (1951).

(9) V. A. Pleskov and A. M. Monoszon, *J. Phys. Chem., U.S.S.R.*, **4**, 696 (1933).

(10) C. B. Hurd, E. W. Engel and A. A. Vernon, This Journal, **49**, 447 (1927).

(11) J. S. Krudl, A. S. Trumin and C. D. Scott, *J. Ceram. Soc.*, **24**, 225 (1941).

Even changing the nature of the ion produced no electrode action in liquid ammonia. In aqueous solutions at a high *p*H other ions, most frequently sodium ions, will take part in the transport of current, causing the well known "sodium error" of glass electrodes. The presence of a large excess of sodium ion in liquid ammonia solution did not produce an electrode response with any of the glasses tested.

Ammonium ions in liquid ammonia are the counterpart of hydronium ions in water: they change colors of *p*H indicators, catalyze solvolysis reactions, are displaced by certain metals and set up potentials with a hydrogen electrode.[9] Glass electrode action might therefore also be expected in liquid ammonia solutions. Nevertheless, there are differences: the heat of solvation of the proton is 17 kcal./mole lower in liquid ammonia than in water, indicating a more stable system in ammonia. The low mobility of ammonium ions in ammonia as compared with hydronium ions shows that there is no "Grotthuss" conduction in liquid ammonia.

Though complete exchange exists between NH_4^+ and NH_3,[12] the dissociation of NH_4^+ into H^+ and NH_3 is very slight. Even in water ammonium ions have not been found to cause glass electrode "errors" such as sodium ions. In terms of Dole's statistical treatment of glass electrode action,[13] the ammonium ion does not appear to have sufficient energy to exchange with the proton on the glass surface. Therefore, it seems plausible that the ammonium ions in liquid ammonia may not be in equilibrium with ions on the surface of the electrode.

Experimental

The Cell.—A cylindrical cell of 70 mm. diameter provided with a large ground glass joint and several smaller joints in the head for the lead-plated platinum reference electrode and glass electrode was used. The inside of the glass electrode was also filled with liquid ammonia and was provided with another reference electrode. The cell was cooled by immersion in a Dewar flask in acetone and Dry Ice.

Measuring Equipment.—A Beckman model G *p*H meter was used for the purpose of detecting *p*H response. A Precision multirange test meter was used for all current measurements. With this meter 0.1 microampere can be detected. A 2400-volt d.c. power supply was placed in series with the cell and the ammeter. When *p*H measurements were attempted the power supply was removed and the *p*H meter inserted.

***p*H Sensitive Glasses.**—Initial studies were confined entirely to Corning 015 type glass. In all cases the *p*H sensitivity of the membranes was first checked in water. The membranes were then subjected to evacuation followed by long periods of immersion in liquid ammonia. This procedure was adopted to ensure complete replacement of the water in the membrane by liquid ammonia.

Membranes composed of *p*H sensitive glasses of different compositions were similarly tested, *i.e.*, Beckman General Purpose glass and Beckman type E.

Measurements and Results.—A power supply of 300 and 2400 v. d.c., respectively, the cell and the microammeter were connected in series. The resistance of the glass membrane was calculated from Ohm's law. Measurements were made in aqueous solution between 6° and 52° for Corning 015 and Beckman general purpose glass and between 25° and 30° for the Beckman type E glass. The resistance for Corning 015 glass varied between 21 megohms at 52° to 1300 ± 200 megohms at 6°. For Beckman General Purpose glass the resistance varied between 9 megohms at 50° and 600 megohms at 7°.

Similar measurements were performed with aqueous alcohol solutions containing 80% of alcohol and containing a small amount of hydrochloric acid. Measurements could now be carried out to −33°, giving a resistance of 2×10^3 megohms for Corning 015 glass and 1.2×10^3 megohms for Beckman General Purpose glass.

In liquid ammonia solutions no current could be observed in the temperature range investigated, −35 to −1°.

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(12) C. J. Nyman, S. C. Fung and H. W. Dodgen, THIS JOURNAL, **72**, 1033 (1950).

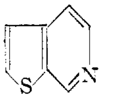
(13) M. Dole, *J. Chem. Phys.*, **2**, 862 (1934).

Sulfur Analogs of Isoquinolines and β-Carbolines. III. The Pomeranz-Fritsch Reaction

BY WERNER HERZ AND LIN TSAI

RECEIVED JUNE 8, 1953

In a previous paper[1] it was demonstrated that isosteres of substituted isoquinolines may be prepared by applying the Bischler–Napieralski reaction to derivatives of thiophene. This work is being extended in our laboratory. It also seemed desirable to investigate the feasibility of synthesizing the parent substances, thieno[2,3-c]- (I) and thieno-[3,2-c]pyridine (II) by means of the Pomeranz–Fritsch reaction[2] inasmuch as 2- and 3-thiophenealdehyde are readily available. A comparison of the properties of these substances with those of isoquinoline would be of great interest.



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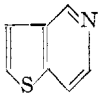
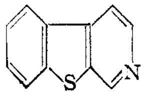


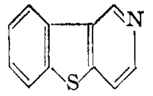
II

Although the condensation of the aldehydes with aminoacetal proceeded with great ease, cyclization of the resulting Schiff bases under the usual conditions gave only small yields of the desired thienopyridines I and II. This seems to be due largely to resinification under the influence of sulfuric acid at the temperatures necessary to effect cyclization. Slightly better yields were achieved by using a mixture of polyphosphoric acid and phosphorus oxychloride as cyclizing agent. To our knowledge this medium has not previously been used in such reactions.

In order to supplement our earlier work on the preparation of sulfur analogs of β-carbolines[3] studies were also carried out which had as their aim the preparation of thianaphtheno[3,2-c]- (III) and thianaphtheno[2,3-c]pyridine (IV) from the aminoacetals derived from 2- and 3-thianaphthenealdehyde. III[4] and IV[5] have since been prepared by different, somewhat less convenient, routes. The cyclization did not proceed in sulfuric acid solution, but using polyphosphoric acid–phosphorus oxychloride the



III



IV

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(1) W. Herz, THIS JOURNAL, **73**, 351 (1951).

(2) W. J. Gensler, *Organic Reactions*, **6**, 191 (1951).

(3) W. Herz, THIS JOURNAL, **72**, 4999 (1950).

(4) H. Kotake and T. Sakan, *J. Inst. Polytech. Osaka City Univ., Ser. C.*, **2**, No. 1, 25 (1951); *C.A.*, **46**, 6121 (1952).

(5) D. B. Capps and C. S. Hamilton, THIS JOURNAL, **75**, 697 (1953).