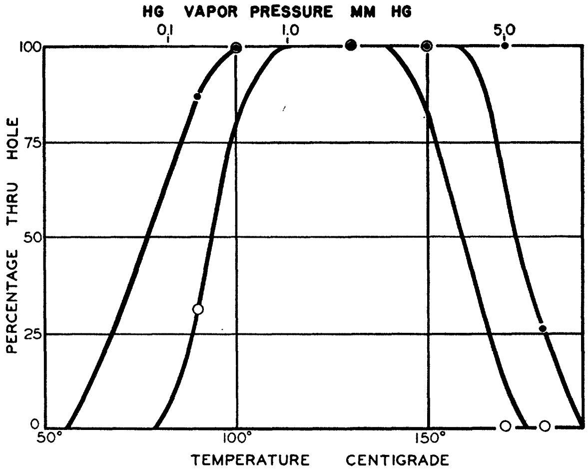

Fig. 3. Increase in the proportion of glow-to-arc transitions through a hole produced by the addition of a 900-mm^2 conducting extension to the cathode. Open circles indicate results obtained without the use of the extension. The small black circles indicate results obtained with one extension connected to the cathode through a 10,000-ohm resistance.

1.5 mm, the breakdown required 1000 v, but the transition was so rapid that the arc appeared to be set up directly.

Although the arc is often established so quickly that no glow appears to precede it, under other conditions the glow is seen to be established with the small portion of the pool within the funnel as a cathode. This area is so small that, with modest currents, an abnormal cathode fall is required for the liberation of the electrons from the cathode. In this case, there is a tendency for the glow to overspread a larger area of the cathode pool in order to reduce the abnormal cathode fall. Ions are present in the vicinity of the pinhole, and they are drawn through it by the potential gradient. A glow is then established in the large, outer portion of the tube. The pool area outside the constriction is sufficiently large that, with the potential difference applied, a relatively large concentration of the current is set up at the hole. Over a considerable range of vapor pressures, this provides the conditions needed to establish the arc along this path.

The efficiency of the process would be expected depend not only on the size of the hole but also on the cathode area outside the funnel. This has been verified by experiments performed with the tube shown in Fig. 1. As the drawing shows, this tube is provided with two conducting areas, *C* and *C′*, that were made by painting the inside wall of the tube with a platinum alloy. Each of the two areas is provided with a lead-out wire by means of which it may be electrically connected to the cathode *K*. If this connection is made directly, the cathode spot is most likely to be set up on the platinum alloy, and the conditions in this case differ enough that comparisons with data in which the spot is established somewhere on the mercury pool may not be justified. To avoid such criticism, the platinum alloy areas have been connected to the cathode through a resistance of about 10,000 ohms. This resistance is high enough to prevent the formation of the cathode spot on the platinum alloy, but it is low enough to permit the alloy to serve as additional cathode area for the glow discharge passing through the pinhole.

The results obtained show that the connection of the platinum area to the cathode through the resistance generally increased the ratio of the number of times that the cathode spot was set up on the annular area of the mercury pool to the number of times that it was set up within the funnel. The data obtained are plotted in Fig. 3; the lower curve was obtained without either of the platinum areas, and the upper curve was obtained by using the single platinum alloy area nearest to the cathode pool. It was also verified that the addition of the second patch raised the curve somewhat.

References

1. C. W. Lufcy and P. L. Copeland, *J. Appl. Phys.* **16**, 740 (1945).
2. P. L. Copeland, *Rev. Sci. Instr.* **16**, 154 (1945).

21 February 1955.

Communications

Demonstration of the Basicity of Water in Alcoholic Solutions

Experiments either designed or interpreted as determining the relative basicity of water versus alcohols have given contradictory answers. Hammett (*1*) points out that because charged acids such as ammonium ion have smaller pK_a values in ethanol than in water, one may conclude that the former is the more basic solvent. On the other hand, the same author cites references to colorimetric and acid catalyzed reactions that indicate the reverse. Hine and Hine (*2*), in reviewing the literature on both the relative acidity and basicity of water versus alcohols, also show that these evaluations depend on the system chosen for study.

The simplest way of assessing the relative magnitude of a given property of two substances is through a competitive situation. In studying the solvochromism (*3*) of alcoholic solutions of an indicator composed of propyl gallate and ferric chloride, we observed that the blue color of the chelate was promoted

Table 1. Compounds arranged in order of decreasing basicity.

Alcohol or miscellaneous compound	Indicator	Milliliters of water per 10 ml of solvent	Mole percent water
Isopropanol	2	0.01	0.42
1,4-Butylene glycol	2	0.03	1.5
sec-Butanol	2	0.08	3.9
t-Butanol	2	0.08	4.1
Ethylene glycol	2	0.15	4.4
t-Pentanol	2	0.11	6.2
Ethanol	1	0.03	0.97
n-Propanol	1	0.03	1.2
n-Butanol	1	0.03	1.5
Isobutanol	1	0.03	1.5
Diethyl carbinol	1	0.03	1.8
n-Hexanol	1	0.03	2.1
1,3-Butylene glycol	1	0.05	2.4
2-Ethyl butanol-1	1	0.04	2.7
Isopentanol	1	0.05	3.0
Methanol	1	0.14	3.1
Cyclohexanol	1	0.06	3.4
Propylene glycol	1	0.10	4.0
Triethyl carbinol	1	0.08	6.1
2,3-Butylene glycol	1	0.13	6.1
Acetonitrile	1	0.44	11.4
Ethylene glycol monoethyl ether	1	0.41	18.1
Ethylene glycol dimethyl ether	1	0.50	22.4
Acetone	1	1.07	30.4
Dioxane	1	2.21	51.3

by bases such as ammonia and many common aliphatic, aromatic, and heterocyclic amines whose $p\mathrm{K}_b$ values ranged from 3 to 12. On the other hand, strong protonic acids such as sulfuric, aliphatic and aromatic sulfonic, aromatic phosphonic, as well as Lewis acids like aluminum chloride, acetyl chloride, and acetic anhydride, repressed chelate formation, resulting in yellow solutions. The fact that the addition of between 0.3 to 1.5 volume percent water to various alcoholic solutions of the indicator was enough to bring about chelate formation demonstrates the behavior of water as a proton acceptor in the common alcohols studied.

Table 1 lists the alcohols in order of increasing mole percent of water that is just required to cause the appearance of the blue color of the chelate. It should be noted that the first six alcohols were titrated using an indicator acidified with acetyl chloride. The latter desensitized the indicator so that the blue color of the chelate was not evident in the more basic alcohols before the addition of water.

The indicator solutions were prepared as follows. For indicator 1, 2 gr of anhydrous ferric chloride and 4 gr of propyl gallate were codissolved in 100 ml of glacial acetic acid with the aid of heat. The color of the solution was a deep yellow brown. Indicator 2 was a duplicate of the first, except that 1 ml of acetyl chloride was added to the foregoing recipe. The color of the resulting solution was a yellow orange.

In each titration 3 drops (0.05 ml/drop) of indicator 1 was added to a 10-ml sample of an alcohol. If the resulting solution was yellow or light green, it was titrated to a blue end-point with water. In the case of the first six alcohols that were capable of turning indicator 1 blue without the addition of water, the more acidic indicator 2 was used in the same concentration. All the solvents were chemically dried and distilled. The fraction used boiled over a $\frac{1}{2}^\circ$ range at worst. The average water content of six of the purified alcohols, as determined by the Karl Fischer method (*4*), was 0.05 percent.

Although the number of cases studied is meager, the data indicate a decrease in basicity with increasing molecular weight in a given series of alcohols. Thus, we have the following set of series.

Primary alcohols: ethanol > *n*-propanol > *n*-butanol > *n*-hexanol.
Secondary alcohols: isopropanol > 2-butanol > 3-pentanol.
Tertiary alcohols: *t*-butanol > *t*-pentanol > triethyl carbinol.

Methanol is the exceptional case in the primary alcohol series, in that it is much less basic than the other members studied. This anomaly is readily understandable because of the greater electronegativity of hydrogen over an alkyl group attached to a carbon atom. In the primary alcohol series, the decrease in basicity is fairly constant, each succeeding member requiring an increase of 0.3 mole percent water. Although the results show that the order for the isomeric butyl alcohols is *sec*-butanol > *t*-butanol > *n*-butanol, the value of 6.1 for triethyl carbinol against a calculated value of 2.4 for *n*-heptanol indicates that the order might be different for higher homologs.

A consideration of the extent of hydrogen bonding and the relative electronegativity of hydrogen versus an alkyl group is helpful in interpreting these results. There is some evidence from infrared spectroscopy that the more extensively a carbinol carbon is shielded by alkyl groups, the lower the degree of hydrogen bonding (*5*). It is a reasonable assumption that the basicity should increase with the degree of polymerization, because the acidic protons are held more tightly, thus offering less competition to an incoming proton. The order of basicity of the polymeric state of the alcohols should be primary > secondary > tertiary. On the other hand, because of the greater electronegativity of hydrogen compared with an alkyl group, the order of basicity in the monomeric state should be the reverse. The order in the isomeric butyl alcohols indicates that these effects are of comparable magnitude. However, in the butylene glycols, the order is 1,4-butylene glycol > 1,3-butylene glycol > 2,3-butylene glycol. Here, the extent of hydrogen bonding seems to be the controlling influence. It should be noted that the order of decreasing basicity is the same as that of decreasing boiling point, another property whose magnitude is greatly influenced by the extent of hydrogen bonding. The same explanation suggests itself for the differences in the basicity and boiling point between ethylene and propylene glycols. The decrease in basicity with chain length in the monohydric alcohols follows from the increased forces between longer chains which in turn weakens the hydrogen bonds.

A few other compounds are cited in Table 1 in order to relate the basicity of the alcohols to other functionalities by the same yardstick.

We have found that indicator 1 is analytically useful for detecting water in alcohol samples. For example, "anhydrous," shelf samples of ethanol gave a light green color with this indicator. The water content was 0.3 to 0.5 percent and was found to be suitable for malonic ester condensations.

SAUL SOLOWAY
PERRY ROSEN

Department of Chemistry, City College of New York, New York, N. Y.

References

1. L. P. Hammett, *Physical Organic Chemistry* (McGraw-Hill, New York, 1940), pp. 260–262.
2. J. Hine and M. Hine, *J. Am. Chem. Soc.* **74**, 5267 (1952).
3. S. Soloway and P. Rosen, *Science* **121**, 3134 (1955).
4. S. Siggia, *Quantitative Organic Analysis via Functional Groups* (Wiley, New York, 1949), pp. 66.
5. L. N. Ferguson, *Electron Structures of Organic Molecules* (Prentice-Hall, New York, 1952), chap. 9.

11 March 1955.

Effect of Isonicotinic Acid Hydrazide on Some Plant Systems

Several months ago Wort (*1*) described some effects of the antitubercular compound isonicotinic acid hydrazide (INH) on the growth of certain higher plants when it was applied to the foliage of established seedlings. General retardation of top growth was observed with INH concentrations of 0.4 to 1.6 percent. INH solutions of the same concentrations applied to the soil similarly caused stunting, except at the 1.6-percent level, which was lethal to several species. Wort went further and showed that in oats, beans, and sugar beet seedlings, leaf catalase and phosphatase activities were depressed, although only slightly, by treatment with 1.2-percent INH (87 μM/ml).

Wort's experiments might suggest that plants are not particularly responsive to this compound, a conclusion that would be at variance with observations on other plant systems that are affected by far lower concentrations of INH. In 1952 Schopfer *et al.* (*2*) showed that a concentration of INH as low as 0.0039 percent in the medium would cause 50-percent reduction in elongation of pea roots in sterile culture, and that this effect was partially reversible by indoleacetic acid. Bustinza and Santamaria (*3*) reported that germination of seeds of *Raphanus sativus, Triticum compactum,* and *Lupinus alba* was completely prevented by 0.4-percent INH and that some inhibition of seedling development in these three species was evident at 200, 50, and 10 ppm, respectively (1.5 μM/ml, 0.36 μM/ml, and 0.07 μM/ml). On the other hand, Nickell and Findlay (*4*), using *Lemna minor* as the test system, found substantial stimulation of growth by 1 to 20 ppm INH (0.007 to 0.15 μM/ml, approximately) but did not record the effects of higher concentrations.

In experiments in these laboratories (*5*) this compound INH has been observed to be an active inhibitor of root growth. In aerated water cultures the roots of Moore barley seedlings grown for 5 days in the dark were inhibited to the extent of 50 percent on a dry weight basis by 350 ppm (2.55 μM/ml) INH presented 24 hr after the seeds were moistened. The roots, although not proportionately reduced in length, were distinctly yellow in color.

Similarly in the cucumber germination test of Ready and Grant (*6*), the elongation of the primary root of cucumber var. Early Fortune at 25° was inhibited 50 percent by a concentration of INH of 225 ppm (1.6 μM/ml). The response curve for Moore barley was almost coincident with that for cucumber at low INH concentrations, with the 50-percent inhibition point occurring at 220 ppm. Root elongation of Koto flax, however, was more sensitive to this compound. Fifty-percent inhibition was observed at 37 ppm (0.27 μM/ml). It is perhaps worthy of comment that in these root responses INH is about one-fifth as active as maleic hydrazide, which has found some uses as a growth regulator and growth repressant.

Top application of INH to young Black Valentine bean plants, either as droplets containing 50 or 100 μg to the base of a unifoliate leaf, or by immersing the unifoliate leaf in a solution of either $1 \times 10^{-3} M$ or $1 \times 10^{-4} M$ for 48 hr did not result in any detectable growth repression or morphological change. Only at much higher levels of application was growth repression evident, as is reported by Wort (*1*).

Thus it appears that INH, like numerous other compounds, has physiological potency in the inhibition of root growth and development at levels substantially lower than those that elicit any morphological responses in the tops of established plants. It is perhaps from the ranks of such compounds that materials suitable for preemergence weed control should be sought.

A. G. NORMAN

Department of Botany,
University of Michigan, Ann Arbor

References and Notes

1. D. J. Wort, *Science* **120**, 72 (1954).
2. W. H. Schopfer, E. Grob, G. Besson, *Arch. sci.* (*Geneva*) **5**, 5 (1952).
3. F. Bustinza and M. L. C. Santamaria, *Antibiotics & Chemotherapy* **3**, 793 (1953).
4. L. G. Nickell and A. C. Finlay, *J. Agri. Food Chem.* **2**, 178 (1954).
5. This article is paper No. 5 from the Plant Nutrition Laboratory, Michigan Memorial Phoenix Project No. 32, of the University of Michigan.
6. D. Ready and V. O. Grant, *Botan. Gaz.* **109**, 39 (1947).

21 March 1955.