Properties and Value of 1,1-Diureido Isobutane (IBDU) as a Long-Lasting Nitrogen Fertilizer

O. R. Lunt and S. B. Clark

The rate-limiting step in conversion of IBDU to plant-available forms appears to be dissolution of IBDU. The rate of this process is not mediated by microbial activity. Hydrolysis of soluble IBDU to urea and then to NH_3 occurs readily under most soil conditions. Particle size strongly influences dissolution rates, smaller particles dissolving more rapidly. Plants make effective use of IBDU to pH ranges from below 5 to above 8. However, conversion of IBDU to urea and NH_4^+ or NO_3^- does not occur as readily under alkaline conditions. The effect does not appear to be large enough to present a serious problem in using IBDU in soils up to at least pH 8.3. Very high rates can be incorporated into soils—up to 32 lbs. of N per 1000 square feet—without important detrimental effects. Plant response indicates a relatively steady supply of nitrogen from IBDU for one or two months, or longer, if large applications are made or relatively coarse granules are used.

The compound 1,1-diureido isobutane (32% N) is readily produced as a condensation product of urea and isobutyraldehyde in acid solution as follows:

$$(CH_3)_2CHCHO + 2(NH_2)_2CO \rightleftharpoons H_2O + (CH_3)_2CHCH(NHCONH_2)_2$$

Interest exists in 1,1-diureido isobutane (isobutylidine diurea or IBDU) as a long-lasting fertilizer, both in this country and abroad. Hamamoto (1966) has described in considerable detail the preparation and physical properties of IBDU and reported on some agronomic experience in Japan. There has been, however, relatively little research reported on its performance in well-defined cropping situations and its reactions in soils. The studies reported here were designed to elucidate its mode of action and characteristics as a long-lasting fertilizer.

According to Hamamoto (1966), IBDU has a solubility in water at pH 7 and room temperature of 0.1 to 0.01 gram per 100 ml. In solution it spontaneously hydrolyzes to the aldehyde and urea. Urea may be directly adsorbed or become available to plants by enzymatic hydrolysis or by microbial mediated enzymatic hydrolysis to ammonium which, in turn, may be oxidized microbially to nitrate. The conversion of urea to these plant-available forms normally occurs rapidly in soils capable of supporting plant growth (Alexander, 1961; Skujins, 1967; Chin and Kroontje, 1963). The rate-limiting step in the conversion of IBDU to plant-available forms is considered by Hamamoto (1966) to be the rate of dissolution. This rate is increased by smaller size granules, lower pH, higher temperature and higher soil moisture.

PROCEDURES

Experiment 1. The following study was devised to determine whether hydrolysis of IBDU is microbially mediated or occurs spontaneously in soils, and to obtain some measure of the effect of temperature and particle size on dissolution rates. IBDU in two sizes (0.24 to 0.15 mm. and 1 to 2 mm. diameter) was blended into Yolo loam, pH 6.2, at the rate of 10 mg. per 20 grams of soil. With the objective of assuring innoculation of the soil with organisms which use IBDU as a substrate, approximately 10 per cent of the soil used was taken from plots which three months before had received a dressing of IBDU.

The 20-gram soil samples to which IBDU had been added were individually mixed with 60 grams of coarse sand and placed in bottles containing 12 ml. of water or 10 ml. of water and 2 ml. of toluene. One set of treatments was incubated in a room at 50° F. (10° C.) and the other in a room at 80° F. (27° C.). Each treatment was replicated three times. The non-sterile treatments were fitted with caps having a polyethylene window which permits gas, but not water vapor, exchange. The incubation and extraction procedure was essentially that described by Bremner (1965). After 14 days, treatments were extracted with 2*N* KCl and total soluble nitrogen in the extract was determined. Urea in the extract was enzymatically hydrolyzed after which NO_3^- and NO_2^- were reduced and NH_3 distilled over for analysis by titration.

Experiment 2. In order to ascertain the effect of soil pH on solubilization rates, granular IBDU in two particle sizes, *i.e.*, 0.6 to 1.4 mm. and 2.4 to 2.8 mm. diameter, was blended into samples of Yolo loam which had been adjusted to various pH values, *i.e.*, 3.3, 4.8, 7.2, and 7.8. Rates equivalent to surface applications of 8 and 32 lbs. of N per 1000 square feet were used. The samples were incubated for 19 days at a moisture content of 14.0% (approximately "field capacity"). Under these conditions, aeration would be expected to be adequate. At the end of this period, the soil pH was redetermined and the samples were extracted as described in Experiment 1 and analyzed for $CO(NH_2)_2$, NO_3^-, NO_2^-, and NH_4^+.

Experiment 3. In view of the effect of pH on the mineralization of IBDU observed in Experiment 2, a cropping study was devised to determine if soil pH is likely to be a significant factor in crop response to IBDU. The pH of Yolo loam (initial pH 6.2) was adjusted from an acid to an alkaline range by thoroughly blending powdered $FeSO_4 \cdot 7H_2O$ into one kilogram of dry soil at rates of 7 or 21 grams per kilogram or dolomitic limestone at rates of 12 or 24 grams per kilogram. The soils were moistened, mixed several times, and stored for five days. At the end of this period, pH values of the saturated paste measured 4.0, 5.8, 7.2, and 8.2 for the various treatments. Fourteen hundred grams of soil were placed in containers of appropriate size, and IBDU of particle size

Department of Botanical Sciences, University of California, Los Angeles, Calif. 90024

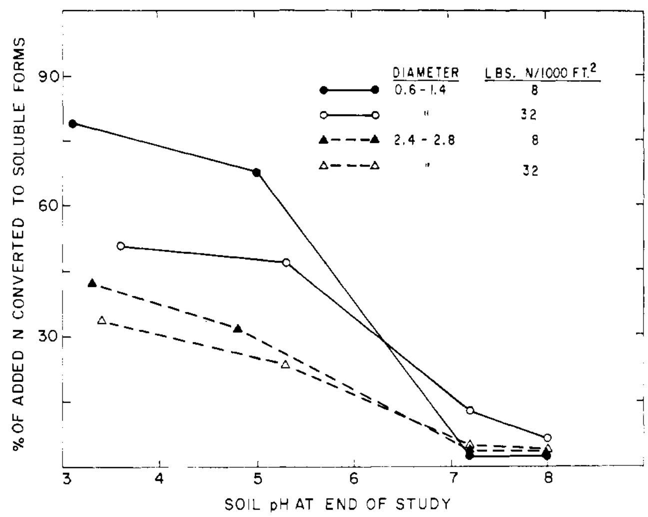

Figure 1. Percentage of added IBDU converted to soluble forms ($CO(NH_2)_2$ + NH_4^+ + NO_3^- + NO_2^-) as influenced by soil pH and particle size of fertilizer

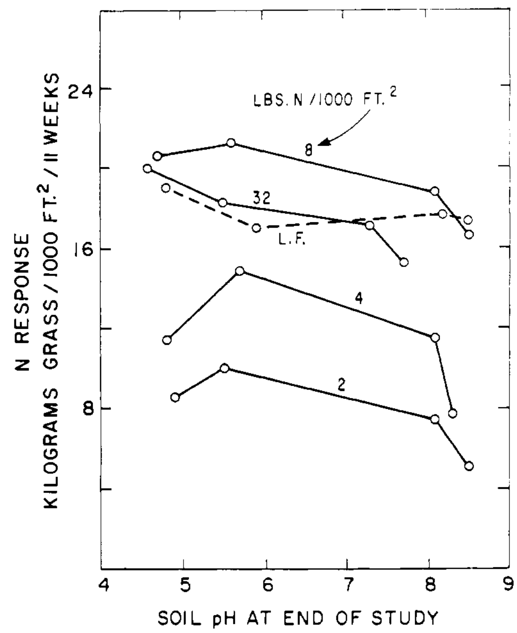

Figure 2. Response of grass to various rates of IBDU on 4 soils ranging in pH from below 5 to greater than 8

0.6 to 1.4 mm. diameter was blended into the soil at rates of 2, 4, 8, and 32 lbs. of N per 1000 square feet. An appropriate number of pots received no fertilizer or were reserved for semi-weekly application of Hoagland's No. 2 nutrient solution, containing 15 meq. of N per liter.

The pots were seeded to Alta Fescue and irrigated twice or three times weekly at rates that permitted about 35% of the applied water to leach through the container. After the third week, the grass was clipped weekly to 1½ inches and the clippings were quantitatively collected, dried, and weighed through a period 11 weeks after seeding. Each treatment was replicated three times. Thus, there were 72 pots in the factorial study involving 4 pH levels and 6 rates or sources of nitrogen.

RESULTS AND DISCUSSION

Conversion to Plant-available Forms. The results of the incubation study on the conversion of two particle sizes of IBDU to urea, ammonium and nitrate, under sterile and nonsterile conditions at two temperatures, *i.e.*, 50° and 80° F., are summarized in Table I. Several conclusions are evident. The quantity of IBDU converted to the sum of urea, ammonium, and nitrate is seemingly substantially independent of microbial activity. This indicates that dissolution and hydrolysis of IBDU to urea under these conditions was not microbially mediated. There was a moderate enhancement of solubilization by temperature. There was a clear-cut effect of particle size on conversion to soluble forms. These data are qualitatively consistent with Hamamoto's (1966) contention that the rate of dissolution of IBDU is the limiting factor controlling its conversion to plant-available forms. While the hydrolysis of urea and oxidation of ammonia are undoubtedly objects of microbial activity when IBDU is used in soils, the fact that the rate-limiting step in its conversion to these plant-available forms is independent of microbial activity distinguishes IBDU from urea-formaldehyde, which appears to be largely dependent on biological attack for conversion to plant-available forms (Corke and Robinson, 1966). The modest effect of temperature on conversion to available forms suggests the material would be relatively effective in cool weather, as compared to nitrogenous materials which require microbial degradation. The data indicate that, when incorporated into soil, conversion to plant-available nitrogen would require from about one to two months, or longer, for the particle sizes used. This duration of nitrogen supply would be advantageous in numerous cropping situations. The effect of particle size on solubilization also provides a means of controlling availability rates.

Table I. Conversion of IBDU-N to Soluble Forms as Influenced by Particle Size and Environmental Conditions

IBDU Size Diameter, mm.	Incubation Conditions	% of Added N from IBDU Converted to Urea, Ammonium & Nitrate	
		50° F.	80° F.
0.15–0.24	Nonsterile	35	45
0.15–0.24	Sterile	32	43
1–2	Nonsterile	21	25
1–2	Sterile	19	24

pH Effects. The results of the second experiment, summarized in Figure 1, show soil pH has a pronounced effect on conversion to soluble forms, *i.e.*, $CO(NH_2)_2$, NO_2^-, NO_3^-, and NH_4^+. The reduction in conversion to soluble forms at high pH is so pronounced that the question of the effectiveness of IBDU in alkaline soils is pertinent.

The results of the third experiment are summarized in Figure 2. *The increase* in grass yield for the 11-week period after fertilization, over the unfertilized treatments, is plotted against the pH of the saturated paste at the termination of the study. Yields for the unfertilized plots were 7.0, 9.4, 10.1, and 12.2 kilograms of dry grass per 1000 square feet at final soil pH values of 5.1, 5.7, 7.8, and 8.1. It will be noted that pH values of the most acid treatment rose about 0.8 of a pH unit during the course of the study, as did the soil originally at 7.2 on most nitrogen treatments. Maximum yields were obtained at 8 lbs. of N per 1000 square feet from IBDU. These yields, in general, were usually a little better than the liquid fertilizer treatment which was intended to be an optimum management program. The 32-pound rate of application was slightly lower, in general, than the 8-pound application rate, possibly because of slight toxicity from sustained high levels of NH_4^+ produced from urea hydrolysis. The appearance of grass on this treatment was comparable in every respect with the 8-pound treatment, and it may be considered that toxicity from the exceptionally high application rate of 32 lbs. of N from IBDU, under the conditions of this experiment, was very minor.

The principal objective of this study was to ascertain if soil pH exerts an important effect on the plant response to given amounts of IBDU. This is most clearly observed where nitrogen application rates did not produce maximum yields, *i.e.*, the 2- and 4-pound application rates. There is an interaction between pH and the effectiveness of the applied nitrogen. The response at pH 5.6 was almost twice that observed at about pH 8.4 for the lower N rates. Nitrogen from IBDU was also more effective at pH 5.8 than 4.8. This was due presumably to acid soil toxicity more than offsetting the larger supply of N at the latter pH value. The percentage yield depression at high pH became quite small at the higher nitrogen rates. The yield responses, thus, confirm that availability of N from IBDU is somewhat depressed at alkaline pH values, particularly those about 8, but the effect is much less than would be expected by the hydrolysis observed in incubation studies. The observed disparity may be due to localized effects of pH induced by respiration of the roots. It is also possible that localized pH effects attributable to clays become more prominent under cropping than non-cropping conditions. Hydrogen ion activity on clay surfaces is reported to be as much as 100 times greater on the surface of clays than in the ambient solution (Harter and Ahlrichs, 1967).

Effect of IBDU on Soil pH. IBDU would be expected to produce an initial increase in soil reaction as urea hydrolyzes to NH_3. Subsequently, acidulation would be expected if conditions permit the oxidation of NH_4^+ to NO_3^-—4 moles of H^+ being produced for each mole of NH_4^+ oxidized. Data from the second experiment showed the following pH values after 19 days incubation (particle size 0.6 to 1.4 mm., initial pH 4.8): 4.7, 5.0, 5.4, 6.4, and 7.2 for N applications of 0, 4, 8, 16, and 32 lbs. per 1000 square feet, respectively. In a slightly alkaline soil, pH 7.4, changes were no more than 0.1 unit from the same application rates in that time interval. In the third experiment, after eleven weeks of cropping, pH values were generally slightly lower. A treatment receiving no nitrogen had a pH of 5.1, while the pH dropped to 4.6 when 32 lbs. of nitrogen from IBDU had been used.

Management Considerations. Maximum safe application rates as well as the time required for complete mineralization are important IBDU characteristics for management programs. Considering the latter question first, as previously noted, the data of Table I indicate about one to two months would be required for mineralization of IBDU with the particle sizes used. The yields obtained in Experiment 3 showed that 2 pounds of N per 1000 square feet from IBDU maintained grass yields at about maximum levels for six weeks, while the 4-pound rate maintained yields very well until the 9th or 10th week. These results are thus consistent with expectations from incubation studies. Very large applications have maintained grass yields much longer.

Maximum safe soil incorporation rates are very high for IBDU, as shown by Experiment 3 where 32 pounds of N per 1000 square feet were mixed into soil with negligible detrimental effects on plant growth. This is 5 to 10 times higher than is safe with conventional materials. Where surface applications have been made on turfgrass, occasionally chlorosis has been observed to develop about three weeks after application where rates reached about 6 pounds of N per 1000 square feet or higher. The injury did not resemble soluble salt injury and seemed to be associated with heavy morning dews. It is believed that repeated absorption of solution products of IBDU through plant tissues resulted in a physiological disorder, possibly due to ammonia, causing chlorosis. Tissue levels of N associated with chlorosis were abnormally high, reaching 6 to 7%.

Except for the chlorosis problem, the characteristics of IBDU seem to be well adapted for use where long-lasting, controlled-availability nitrogen sources are advantageous.

LITERATURE CITED

Alexander, M., "Introduction to Soil Microbiology," pp. 258–9, Wiley, New York, 1961.
Bremner, J. M., *Am. Soc. Agron.* **2,** pp. 1339–41 (1965).
Chin, Wei-Tsung, Kroontje, Wybe, *Soil Sci. Soc. Amer. Proc.* **27,** 316–18 (1963).
Corke, C. T., Robinson, J. B., *Nature,* **211,** No. 5054, 1202 (1966).
Hamamoto, M., *Proc. Fertiliser Soc.,* **90,** 1–77 (1966).
Harter, R. D., Ahlrichs, J. L., *Soil Sci. Soc. Amer., Proc.* **31,** 30–3 (1967).
Skujins, J. J., "Soil Biochemistry," p. 371, Marcel Dekker, N. Y., 1967.

Received for review July 19, 1968. Accepted July 9, 1969. These studies were supported in part by a grant from the Mitsubishi Chemical Company, Tokyo, Japan, and the Department of Botanical Sciences, University of California, Los Angeles, Calif.