Effect of Structure on Nitrification of Urea Derivatives
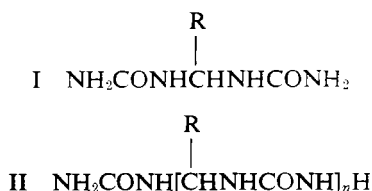
J. T. Hays and W. W. Haden

Reaction of urea with formaldehyde gives the commercial ureaforms; reaction with higher aldehydes gives products which release nitrogen more rapidly and completely than ureaforms due to their lower molecular weight and their susceptibility to hydrolysis by soil moisture. A series of symmetrical dialkylmethylenediureas has been prepared for comparison as controlled release nitrogen fertilizers. As the alkyl substituents were varied from C_1 to C_4, the solubility and rate of nitrification both decreased. Nitrogen release was relatively complete and uniform. Time for complete release varied from 12 to 15 weeks for the dimethyl and diethyl compounds to about one year for diisopropyl-methylenediurea. The observed effects on nitrification were not due merely to substitution on terminal urea groups, since the corresponding 1,3-dialkylureas, with the exception of the dimethyl compound, were resistant to nitrification and exerted an inhibiting effect.

Chemical modification of urea to give products of reduced solubility and reduced nitrogen availability has been one of the most successful approaches to production of controlled release nitrogen fertilizers. Best known materials of this type are the commercial ureaforms which consist of mixtures of polymeric methyleneureas (Hays et al., 1965) formed by condensation of urea with formaldehyde. The condensation of urea with other aldehydes has also been extensively studied and has yielded products of both theoretical and practical interest. Aldehydes used have included acetaldehyde (Scheffer et al., 1956, 1957), propionaldehyde (Hamamoto, 1966; Schäfer, 1963a,b), n-butyraldehyde (Schäfer and Kalk, 1965a,b), isobutyraldehyde (Hamamoto, 1966; Schäfer and Kalk, 1965a,b), crotonaldehyde (Jung, 1961a,b), furfural (Hamamoto, 1966), and glyoxal (Symes and Loveless, 1962).

These products consist mainly of alkylidenediureas (I) with limited amounts of higher condensates (II), with very low values for n (Hamamoto, 1966; Scheffer et al., 1956, 1957).

$$\begin{array}{c} R \\ | \\ \text{I} \quad NH_2CONHCHNHCONH_2 \end{array}$$

$$\begin{array}{c} R \\ | \\ \text{II} \quad NH_2CONH[CHNHCONH]_nH \end{array}$$

The products from crotonaldehyde and glyoxal have cyclic structures in which free amide groups in I appear to have undergone further reaction with a double bond or carbonyl in the R-groups.

The condensation products of urea with higher aldehydes are generally reported to release their nitrogen more rapidly and completely than the ureaforms (Hamamoto, 1966; Schäfer and Kalk, 1965a,b; Scheffer et al., 1956, 1957). The low molecular weights of such materials would be expected to make them readily susceptible to biological breakdown. In addition, the condensates of urea with acetaldehyde, propionaldehyde, isobutyraldehyde, and furfural hydrolyze very readily in soil. Miyazaki [(1965); reviewed in detail by Hamamoto (1966)] found that these condensates gave relatively complete breakdown to urea in sterilized soil in two weeks at 29° C. The pronounced effect of soil moisture on the mineralization of isobutylidenediurea reported

by Hamamoto (1966) is attributed to the sensitivity of this compound to hydrolysis. Mineralization studies or crop tests showing rate of nitrogen release from these urea-aldehyde condensates have thus measured both biological and hydrolytic breakdown. The susceptibility to hydrolysis introduces complications in their use as fertilizers; increased particle size and granulation with other fertilizer components (Hamamoto, 1966) provide a measure of protection against rapid nitrogen release under heavy rainfall or irrigation.

In contrast to the higher alkylidenediureas, methylenediurea (I, R = H), formed by reaction of urea with formaldehyde, is much less susceptible to hydrolysis. In the Miyazaki experiments, methylenediurea gave no urea in sterilized soil. However, it readily undergoes biological conversion to nitrate (Hays and Haden, 1966). We have prepared a series of symmetrical dialkylmethylenediureas with the expectation that these would show lower solubility and reduced availability of nitrogen while preserving the resistance of the methylenediurea structure to hydrolysis and its susceptibility to biological breakdown. The corresponding symmetrical dialkylureas have also been compared with the methylenediureas.

MATERIALS

Methylenediurea. Hays and Haden (1966).

Isobutylidenediurea. Mitsubishi Chemical Industries, Japan.

Nitroform. Hercules Inc. (Hays and Haden, 1966).

1,1'-Methylenebis[3-alkylureas] were prepared by reaction of the alkylurea with formaldehyde in the presence of acid following the procedure for 1,1'-methylenebis[3-methylurea] (Kadowaki, 1936). Nitrogen analyses are given in Table I; melting points were in agreement with literature values.

1,1'-Methylenebis[3-isopropylurea] appears to be a new compound; m.p. 210–12° C.

Analysis. Calcd. for $C_9H_{20}N_4O_2$: N, 25.9%. Found: N, 25.8%.

1,3-Dialkylureas. Nitrogen analyses in Table I.

1,3-Dimethylurea. (Matheson, Coleman, and Bell, Practical), recrystallized from methanol; m.p. 107–9° C.

1,3-Diethylurea. Aldrich Chemical Co.

1,3-Di-n-propylurea. Prepared from n-propylamine (Eastman White Label) and n-propylisocyanate (Carwin Organic Chemicals) by reaction in benzene, cooling, and separating the precipitate; m.p. 104.5–106.5° C.

1,3-Diisopropylurea. Prepared from isopropylamine (Eastman White Label) and isopropylisocyanate (Ott Chemical
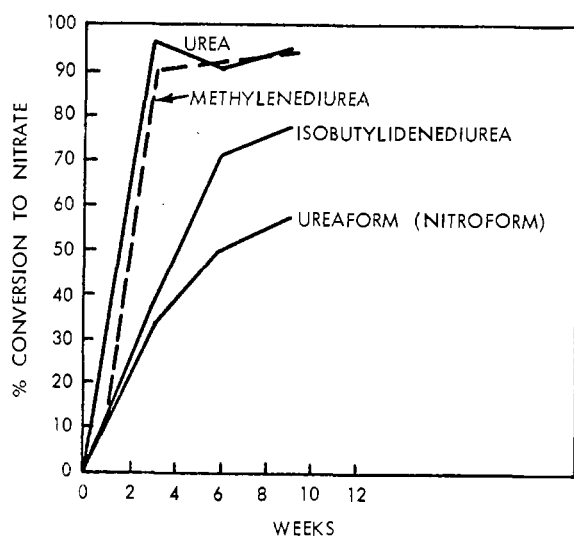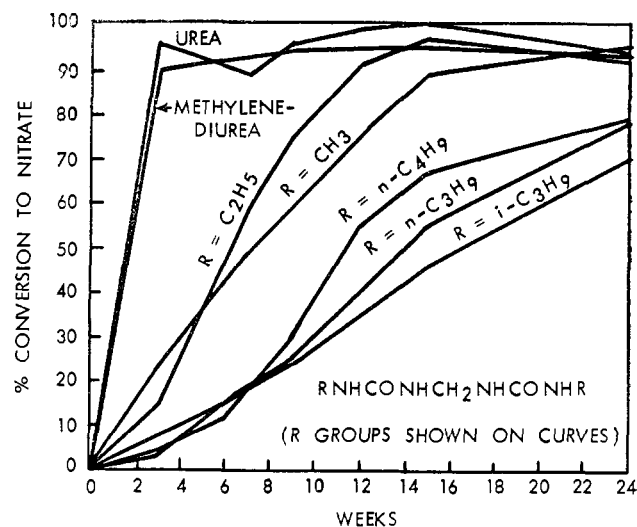
Figure 1. Nitrification of alkylidenediureas

Figure 2. Nitrification of dialkylmethylenediureas

Co.) in the same manner as 1,3-di-*n*-propylurea; m.p. 193–4° C.

1,3-Di-*n*-butylurea. Prepared from *n*-butylamine (Matheson, Coleman, and Bell, Practical) and *n*-butylisocyanate (Ott Chemical Co.) by refluxing 1 hour in benzene, cooling, and filtering; m.p. 71–4° C.

Isopropylurea. Aldrich Chemical Co.

Soil. The soil used in the nitrification studies was taken from Delaware farm land which had not been recently fertilized. It was a sandy clay loam (58% sand, 14% silt, and 28% clay) containing 0.98% organic matter. The pH (originally 6.1) was adjusted to 7.1 with calcium oxide before use and buffered with calcium carbonate (Clark *et al.*, 1959).

PROCEDURES

Nitrification. (Clark *et al.*, 1959; Hays *et al.*, 1965). In this paper, the term nitrification has been used to cover the combined processes of ammonification and oxidation to nitrate; strictly speaking, it applies only to the latter reaction.

RESULTS AND DISCUSSION

Nitrification of Alkylidenediureas. Data on conversion to nitrate on incubation with soil at 30° C. (Figure 1) show the rapid biological availability of methylenediurea nitrogen

Table I. Solubilities and Analyses of Urea Derivatives

Derivative	% N	% WIN	% HWIN
Dialkylmethylenediureas (III)			
R:			
H	41.7	0.55	...
CH₃	34.6	...	...
C₂H₅	29.6	3.9	0.1
n-C₃H₇	25.8	19.0	1.2
i-C₃H₇	25.8	19.0	4.9
n-C₄H₉	22.8	21.4	16.2
Dialkylureas (IV)			
R:			
CH₃	31.5	...	...
C₂H₅	23.9	...	...
n-C₃H₇	19.2	3.3	2.8
i-C₃H₇	19.0	10.0	2.3
n-C₄H₉	16.1	14.3	10.1
Isopropylurea	27.7		

and the somewhat slower availability of isobutylidenediurea (in the absence of hydrolysis conditions). This behavior is typical of the alkylidenediureas which generally give release rates intermediate between the rapid release for urea and the more gradual release from ureaforms.

Methylenediureas. The reaction of monoalkylureas with formaldehyde was used to prepare the symmetrical dialkyl-methylenediureas (III).

III RNHCONHCH₂NHCONHR

(R = CH₃, C₂H₅, *n*-C₃H₇, i-C₃H₇, *n*-C₄H₉)
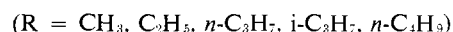
Solubilities are shown in Table I in terms of cold water-insoluble (WIN) and hot water-insoluble nitrogen (HWIN) as determined in the A.O.A.C. (1965) activity index procedure for ureaform fertilizers. Nitrification rates are shown in Figure 2. As the molecular weight of the substituent was increased, the solubility decreased and the rate of nitrification decreased. However, the diethyl compound appeared to nitrify more rapidly than the dimethyl and the dibutyl more rapidly than the dipropyl compounds. While these irregularities are not great, they suggest that the structure of the molecule as a whole, rather than at a point of substitution, determines susceptibility to biological attack.

The dimethyl- and diethylmethylenediureas showed relatively rapid and complete release of nitrogen of the type that might be of interest for agricultural crops. Initial rates for these compounds were comparable to those for ureaforms for about the first six weeks but continued up to complete release in 12 to 15 weeks. However, they would not be resistant to leaching since they are appreciably soluble in water.

The dipropyl and dibutyl compounds started more slowly than ureaforms but reached a comparable level in 24 weeks. These compounds all released their nitrogen at a fairly constant rate. Figure 3 shows data obtained for the diisopropylmethylenediurea in an incubation experiment carried out for 47 weeks. The nitrification rate was surprisingly near a straight line over the entire period and reached the high conversion of 87%. While long term nitrification rates cannot be accepted as quantitative due to lack of control of, or measurement of, denitrification and immobilization of nitrogen in the soil, these results appear to indicate that a single compound tends to give a more uniform rate of release and a more complete release than a polymeric product in which the proportion
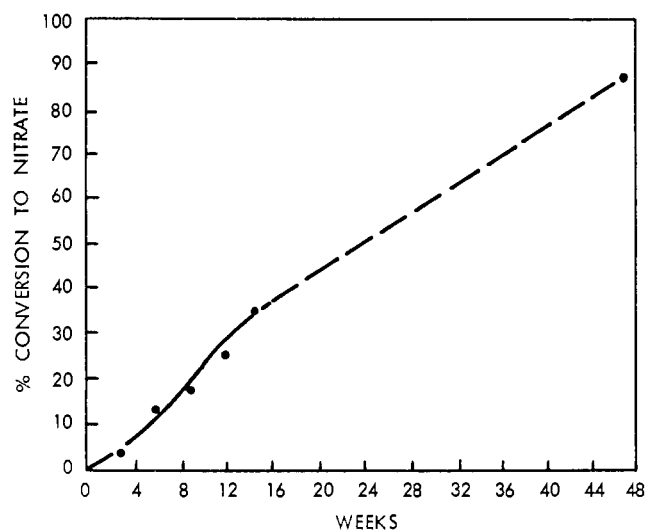
Figure 3. Nitrification of 1,1'-methylenebis(3-isopropylurea)

Figure 4. Nitrification of dialkylureas

of high molecular weight material may increase as nitrification proceeds.

Dialkylureas. The dialkylmethylenediureas (III) are also disubstituted ureas. The corresponding symmetrically substituted dialkylureas (IV) were therefore also subjected to the

IV RNHCONHR

(R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$, n-C$_4$H$_9$)
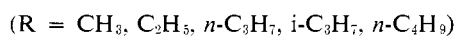
nitrification procedure along with isopropylurea as a monoalkylurea (Figure 4). Nitrifications of isopropylurea and 1,3-dimethylurea were slightly delayed, but then proceeded at approximately the same rate as urea. The higher dialkylureas showed a surprising resistance to attack; not only did they not release their nitrogen but they appeared to decrease the normal release of soil nitrogen (as evidenced by negative nitrification values). Diethylurea (Figure 4) gave negative values for 9 weeks, had begun to nitrify at 12 weeks, and then between 15 and 47 weeks, reached 77% conversion to nitrate. The dipropyl and dibutylureas never reached positive conversions to nitrate; values at 24 weeks were: di-n-propylurea, −33%; diisopropylurea, −5%; di-n-butylurea, −32%. While these effects are not completely understood, it is clear that the 1,3-dialkylureas do not behave in the same way as the symmetrical dialkylmethylenediureas in the nitrification reaction and that the dialkylurea structure alone is not responsible for the release properties of the dialkylmethylenediureas. Another example of the biological activity of certain dialkylureas is their inhibition of urease action as reported by Sor et al. (1966).

CONCLUSIONS

On the basis of the information presented, the following conclusions can be reached in regard to susceptibility to breakdown in soil of various structures in simple urea derivatives.

—CONH$_2$ groups are readily attacked—e.g., in urea, isopropylurea, methylenediurea. The rate depends strongly on solubility—e.g., methylenediurea gives a much more rapid rate than higher methyleneureas in ureaforms.

The methylene structure in the grouping —NHCONHCH$_2$-NHCONH— is readily attacked. The rate is influenced by
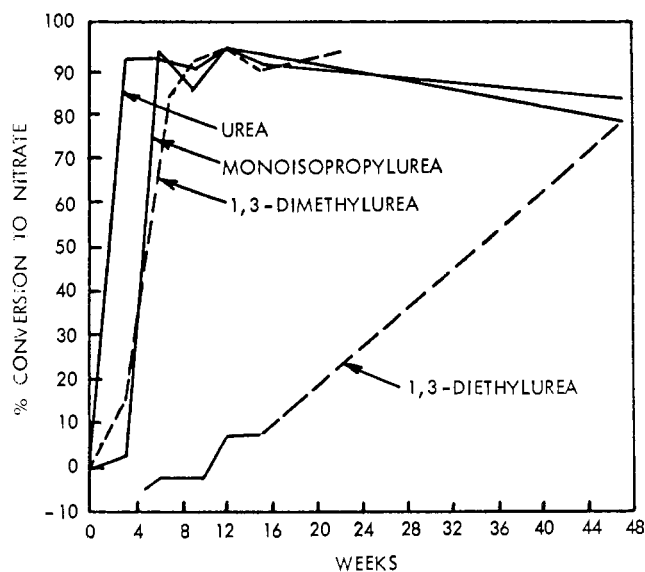
solubility, but is also affected by the specific structure of the molecule.

The structure, RNHCONHR, with the exception of 1,3-dimethylurea, is very resistant to attack and even appears to have an inhibiting effect. This is a structural rather than a solubility effect since the diethyl and dipropylureas do not nitrify rapidly although they are soluble.

ACKNOWLEDGMENT

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