

leads to $I((\text{CH}_3)_2\text{N}) = 9.45$ eV, compared with a value of about 9.1 eV obtained by Gowenlock⁸.

It is possible to assess Foner's value for $I(\text{N}_2\text{H}_3)$ by calculation of the following differences in ionization potentials of isoelectronic radicals:

$$I(\text{NH}_2) \text{ (ref. 2)} - I(\text{CH}_3) \text{ (ref. 9)} = 11.4 - 9.85 = 1.55 \text{ eV}$$

$$I((\text{CH}_3)_2\text{N}) - I((\text{CH}_3)_2\text{CH}) \text{ (ref. 9)} = 9.45 - 7.9 = 1.55 \text{ eV}$$

$$I(\text{N}_2\text{H}_3) - I(\text{CH}_2\text{NH}_2) = 7.9 - 6.25 = 1.65 \text{ eV}$$

It can be seen that the differences between isoelectronic pairs are practically constant, indicating that Foner's value cannot be greatly in error.

Using our value of $A(\text{N}_2\text{H}_3^+) = 11.3$ eV and $I(\text{N}_2\text{H}_3) = 7.9$ eV, a value of $D(\text{H}-\text{N}_2\text{H}_3) = 78$ kcal/mole is obtained.

Unless otherwise stated, thermodynamic values were obtained from the *National Bureau of Standards Circular 500*, Washington, 1952, and *JANAF Thermochemical Tables*, The Dow Chemical Company, Midland, Michigan, up to Quarterly Supp. No. 17, March 1965.

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Effect of pH and Addition of Organic Materials on Denitrification Losses from Soil

WE have reported¹ that added nitrate-nitrogen was lost by denitrification during incubation of soil at moisture levels as low as 20 per cent saturation (20 per cent of the maximum water-holding capacity). For the soil used this saturation level was equivalent to pF 4.2, which is commonly taken as the soil moisture content at which wilting of plants occurs. This loss occurred even in the absence of added organic materials. The results do not agree with a previous report² that denitrification of added nitrate occurred only at moisture levels greater than 60 per cent saturation and then only when decomposable organic materials were added.

In view of the conflicting results it was decided to supplement the results of the previous study¹ by using the same soil and studying the effects of addition of organic materials on the extent of loss of added nitrate over the moisture range from the wilting percentage to waterlogging. In addition, pH was studied as a further variable, as this effect appears to have been studied, as yet, only under waterlogged conditions³.

Samples of the soil were adjusted to different pH levels by addition of varying amounts of calcium carbonate or aluminium chloride, followed by moist storage for 3 months with intermittent leaching. Samples having pH values of 4.7, 6.5 (the original soil) and 8.0 were selected for study. The methods used were as described previously¹, involving 12 weeks' incubation at 28° C after applying the treatments shown in Table 1. Losses of nitrogen were determined by the differences in total nitrogen content initially and at the end of incubation, with due precautions being taken to ensure complete recovery of all organic and inorganic forms of nitrogen in the samples.

Table 1. NITROGEN LOSSES IN SOIL DURING INCUBATION

	pH 4.7			pH 6.5			pH 8.0					
	% saturation	20	50	133	% saturation	20	50	133	% saturation	20	50	133
$\text{NO}_3-\text{N}^\dagger$	Percentage loss of applied nitrate-nitrogen											
" + straw [†]	2.5	4.4	56.9	10.3	21.7	82.4	2.0	24.5	71.6			
" + compost	22.8	47.0	94.9	23.8	44.3	95.7	43.5	58.5	97.6			
L.S.D. ($P < 0.05$) = 5.0 per cent.	31.2	29.7	60.8	24.4	48.0	96.1	9.5	40.2	88.9			

Each result is mean of duplicate treatments.

* 20 per cent, 50 per cent and 133 per cent saturation equivalent to pF 4.2, 2.5 and 0 (waterlogged) respectively.

† 600 p.p.m. (soil basis) as potassium nitrate dissolved in added water.

‡ Ground straw and compost added at 2 per cent w/w (dry soil basis).

The three results obtained in the previous study¹ are included in Table 1 for completeness, namely, losses at pH 6.5 at the three moisture levels in the absence of added organic material. In the absence of added organic material significant losses of nitrogen occurred at all pH levels under waterlogging, at pH 6.5 and 8.0 at 50 per cent saturation, and only at pH 6.5 at 20 per cent saturation. Losses due to addition of organic material (straw or compost) were increased by an average of 26 per cent at 20 per cent saturation, 28 per cent at 50 per cent saturation and 19 per cent under waterlogging. Losses of nitrogen due to addition of straw averaged 13 per cent more than those due to addition of compost, although the differences due to the two materials were consistent only at pH 8.0. In the presence of added organic materials nitrogen losses averaged 48, 55 and 56 per cent at pH 4.7, 6.5 and 8.0 respectively. With straw additions there were no consistent effects of pH on nitrogen losses at the different moisture levels. With compost additions the only consistent trend due to pH was at 20 per cent saturation, where nitrogen losses decreased with increasing pH .

In general, although greater losses of added nitrate-nitrogen occurred under waterlogging than at the two lower moisture levels, the addition of organic materials increased the extent of losses at all moisture levels, but proportionately more so at the two lower levels. The generally greater loss of nitrogen where straw than where compost was added is presumably due to the higher content of readily decomposable substances in the former material resulting in a greater supply of energy for the activity of the denitrifying organisms.

The high nitrogen losses even at pH 4.7 when waterlogged disagree with the results obtained by Bremner and Shaw², who found only small losses below pH 5.0. At any moisture level pH had no consistent effect on losses where organic materials were added. This may be related to the ability of denitrifying organisms to operate over a wide pH range³.

The results obtained indicate that losses of nitrogen by denitrification may occur in the field, where heavy applications of nitrate and organic materials are applied, even at low soil moisture levels, and that the losses may occur over a wide range of soil pH . Whether such losses would be of agronomic or economic significance in comparison with losses of nitrate by leaching can only be determined by field trials.

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Absence of Diffusion Control of Reaction Rate in the Thermal Decomposition of Amorphous Polymers

ONE of the difficulties in the determination of decomposition kinetics of solids by dynamic thermogravimetry is the recognized dependence of the results on procedural variables, particularly sample size and rate of heating^{1,2}.