

Table 1. Oxygen diffusion through three soil cores containing growing corn roots. Calculated as values of ρ (see Eq. 2).

| R (No.) | A (%) | Diffusion rate (10 ⁻⁴ ml/sec) | | |
|------------|----------|---|---------|---------------|
| | | ρ | ρ' | $\hat{\rho}'$ |
| Core No. 1 | | | | |
| 0 | 12.2 | 0.5 | 0.9 | 3.5 |
| 3 | 12.7 | 1.5 | 1.9 | 4.0 |
| 23 | 11.7 | 4.9 | 5.3 | 5.4 |
| Core No. 2 | | | | |
| 0 | 10.5 | 2.2 | 3.8 | 2.8 |
| 0 | 6.5 | 0.2 | 1.8 | 1.1 |
| 3 | 7.7 | 0.9 | 2.5 | 1.9 |
| 6 | 8.0 | 1.6 | 3.2 | 2.3 |
| 18 | 9.8 | 4.1 | 5.7 | 4.1 |
| 35 | 10.1 | 4.4 | 6.0 | 5.8 |
| 47 | 8.2 | 2.4 | 4.0 | 6.0 |
| 58 | 6.6 | 2.8 | 4.4 | 6.3 |
| Core No. 3 | | | | |
| 0 | 7.3 | 1.4 | -0.6 | 1.5 |
| 12 | 9.1 | 5.1 | 3.1 | 3.3 |
| 21 | 9.9 | 7.7 | 5.7 | 4.4 |
| 28 | 10.1 | 9.2 | 7.2 | 5.1 |
| 31 | 10.7 | 9.0 | 7.0 | 5.6 |
| 38 | 10.4 | 9.4 | 7.4 | 6.1 |
| Means | | | | |
| 19 | 9.52 | 3.96 | 4.08 | 4.07 |

($\bar{\rho}, \bar{A}, \bar{R}$). A new regression equation was then calculated from the ρ' .

$$\hat{\rho}' = -1.6 + 0.089R + 0.42A \quad (4)$$

The regression coefficient of R is now significant at $P(0) < 0.005$, while the coefficient of A is still at $P(0) < 0.10$. Figure 2 shows the regression plane and deviations, $\rho' - \hat{\rho}'$. Values of ρ' and $\hat{\rho}'$ are given in Table 1.

To test the importance of the air-filled pores of the root medium for the increased diffusion of oxygen, measurements were made on two additional cores. A layer of water-saturated 0.5-mm glass beads, 1.7 cm thick, was placed below one core with an air space, from which the air could be sampled, above and below the layer. The glass beads were supported by a single sheet of tissue paper on top of a plastic screen. A 0.6-cm layer of soft paraffin wax (rosebush wax) was placed below the other soil core. The meas-

Table 2. Oxygen diffusion through two non-porous media transfixed by corn roots. Calculated in terms of ρ (see Eq. 2).

| ρ (10^{-4} ml/sec) | R (No.) |
|---|------------|
| <i>Water-saturated 0.5-mm glass beads</i> | |
| 0.0 | 0 |
| 1.2 | 17 |
| 0.0 | 48 |
| 0.0 | 56 |
| 0.7 | 65 |
| <i>Soft paraffin wax</i> | |
| 0.0 | 0 |
| 0.5 | 23 |
| 0.4 | 33 |
| 0.8 | 46 |
| 1.2 | 62 |

urements of the rates of oxygen diffusion which were made as roots grew through these layers are given in Table 2. The results are not directly comparable to those in Table 1 because of differences in thickness of the soil core and the bead and wax layers; however, it is apparent that the diffusion rates are greatly reduced through the non-porous bead and wax layers. Evidently, the observed increase in the rate of oxygen diffusion through the soil cores containing roots is a joint effect of the roots and the air-filled pores in the soil.

These data suggest that the effect of the roots on ρ occurs solely because of changes in porosity produced by removal of soil moisture during transpiration. Although not measured, transpiration was probably small because the air around the seedlings was saturated with water vapor. Nevertheless, if it is assumed that the roots were effective only because they changed the soil porosity, then the relations shown in Eq. 5 should hold approximately,

$$\hat{\rho}' = b_1A, \quad A = b_2R, \quad \hat{\rho}' = b_1b_2R \quad (5)$$

where b_1 and b_2 are constants. From Eq. 4, $b_1 = 0.42$ and $b_1b_2 = 0.089$, from which $b_2 = 0.089/0.42 = 0.21$. The regression coefficient of A on R is b_2 and thus may also be calculated from the data in Table 1. The result is $b_2 = -0.013$ which differs in sign and magnitude from 0.21 calculated from Eq. 4. In addition, $b_2 = -0.013$ is nonsignificant with $P(0) > 0.50$. Hence Eq. 5 is not supported by the data and the effect of the roots on ρ cannot be regarded as taking place simply through changes induced in the air-filled pores of the soil.

A more probable explanation for the root effect is as follows. At the low soil porosities maintained in these experiments, most of the air-filled pores are discontinuous and nearly ineffective for oxygen diffusion. When penetrated by roots, these pores are linked up by the continuous system of air space within the root, resulting in an overall increase in oxygen diffusion. In the complete absence of air-filled pores, as in the bead and wax layers, the roots would be much less effective. Evidence for the rapid diffusion of oxygen through roots was obtained by tracer studies with O^{15} (4), which have shown that oxygen within the roots of broad bean, rice, and barley is near exchange equilibrium with the air around the foliage.

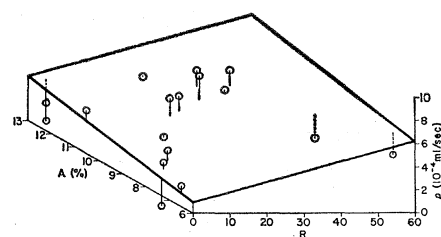


Fig. 2. The regression of ρ' on air-filled pores of the soil A and the number of primary roots R . The regression plane is $\hat{\rho}' = -1.6 + 0.089R + 0.42A$. The deviations, $\rho' - \hat{\rho}'$, are indicated by vertical lines.

Our results together with those of others (4) are of importance because they suggest that roots of terrestrial plants can increase the diffusion of oxygen through the soil without causing changes in the air-filled pores, and that they are not entirely dependent upon the soil for their oxygen supply (5).

CREIGHTON R. JENSEN*

DON KIRKHAM

Department of Agronomy,
Iowa State University, Ames

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* Present address: Department of Soils and Plant Nutrition, University of California, Riverside.

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A Speculation on New Molecules

The remarkable discovery (1) of molecules containing atoms of rare gases leads naturally to the following speculation: it should, in general, be possible to create new molecules from already existing, stable molecules merely by the addition of atoms or "functional groups" by means of appropriate synthetic procedures. This concept is based on the simple observation that the usual, diamagnetic molecule, just as a rare-gas atom, has its electrons in what can be called the "perfect octets" of classical chemistry. In molecular-orbital language the molecule is said to have its electrons filling the lowest avail-

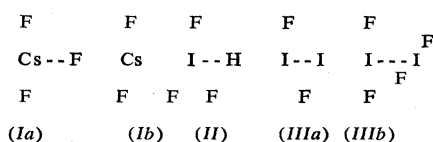
able orbitals—bonding, lone-pair, and so forth—with frequently the first unfilled orbital approximately 9 eV above the highest filled orbital. The first excited state of Xe, $^1P_1(5s^25p^56s)$, is 9.6 eV above the ground state. Thus, whatever conditions govern the formation of molecules from other rare-gas atoms should also govern the formation of molecules from other molecules. Because of the rough successes of the crude calculations in the literature (2) one could fairly safely attribute the bonding in such molecules to the reasonably obvious (3), “delocalized” molecular orbitals and consider the governing molecular parameters to be related to atomic ionization potentials and electron affinities. For those inclined to molecular-orbital computations, it will not be very difficult to perform them by choosing appropriate parameters for any given molecule and following the necessary procedures (see 2). The present speculation is, however, directed more to the synthetic chemist and the spectroscopist than to the theorist, since the existence of these molecules is more interesting than the rationalization of their existence. The chemical reactivity of the molecules is not of present concern. Many of them might be very short-lived as a result of easily induced transitions from one metastable state (that is, molecule) to another more favorable metastable or stable state. Such molecules would be very difficult to observe unless looked for explicitly.

From an examination of the types of rare-gas halides already observed and the theories of their formation, one can conclude that for these molecules the following conditions are significant. (i) The electrons of the central atom should be loosely bound; (ii) the atoms or functional groups attached should be highly electronegative; and (iii) the central atom should be large and the attached groups small in order to avoid the repulsive energy of geometrical crowding. The first two conditions can be expressed jointly as a large negative energy in forming “delocalized” bonds. [Delocalization without promotion is always possible except in the case of two rare-gas atoms. Whether delocalization leads to potential minima or not depends on the first two conditions (4).]

This reasoning indicates that XeF, which has not yet been observed, or XeF₂ is more likely to exist than HeI₂, although of course the net bonding energy must be greater than the net

energy of repulsion. The central atom need only be generalized to a molecule for the conditions to be carried over to the subject of this report.

Consider now the possible molecules



where dashes indicate “localized” bonds. Molecule *Ia* is not likely to exist since, with the CsF molecule largely ionic, the electron to be “delocalized” must be that of the Cs⁺ ion whose ionization potential is 32.5 eV, which is considerably greater than that of Xe, 12.1 eV. Molecule *Ib* is more likely as one could form appropriately polar-symmetry orbitals for the one Cs and three F electrons. Whether there is sufficient bonding energy to be gained with only a single electron contributed from the central atom is a quantitative question not to be decided here. If *Ib* exists, then so should the paramagnetic linear CsF₂. In fact, the latter has the further advantage of not having the probably large F–F repulsions of *Ia* and *Ib*. Molecule *II* is more likely to exist since it has repulsion only with the single electron of the H and the iodine has an ionization potential of 10.4 eV, lower even than that of Xe. Here any “ionic character” of the HI bond with the I negative should enhance the formation of “delocalized” bonds in the plane perpendicular to the HI axis. Molecule *IIIa* only differs from *II* by the F–I repulsions which cannot be estimated a priori. If it exists, though, it is reasonable to suppose that the propeller-shaped (5) *IIIb* will also exist as well as various other complicated multifluorinated derivatives of I₂.

The opportunity for further examples is almost limitless. One might consider how “electronegative” (6) the attached atoms must be; for example, can (HI)O₂ be made? How important are neighbor repulsions (6); for example, can (SnH₄)F₂ be made (6)? Some probably analogous molecules have already been observed, namely, the interhalogen compounds. For example, IF₅ might be an IF molecule (as yet unobserved) with four F’s on the I, and IF₇ might exist as an IF molecule with six F’s, two of which might be attached to the fluorine as well as in a more symmetrical structure. The slightly distorted T-shaped structures of ClF₃ and BrF₃ from microwave spectroscopy data

agree with this picture. PF₅ can be considered as a flattened PF₃ molecule with delocalized binding of the two additional F’s.

Of course in all of this discussion one is still plagued, and will be for some time, by the inadequacy of the whole terminology of the “theory” used to interpret molecular structures. Aside from the molecular orbitals themselves, the ionization potentials and the electron affinities of atoms in molecules are particularly ill-defined quantities. It is thus my own prejudice that any more-than-subjective discussion, pretending to predict the existence or non-existence of proposed molecules, can have little realistic significance at this time.

One might eventually wish to restrict the term “molecule” to those combinations of atoms satisfying some lifetime criterion, since there will be many more quantum-mechanical bound states than there are physically (or rather chemically) meaningful molecules. Unfortunately the more critical problem of molecular stability to intra- or intermolecular rearrangement cannot even be treated subjectively because there is a lack of appropriately crude empirical concepts analogous to those so useful in discussing time-independent molecular properties.

JEREMY I. MUSER

Rockefeller Institute, New York 21

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3. For example, as in crystal or ligand field theory.
4. The molecule LiXe could, in principle, be made by means of the appropriately polar delocalized-bonding (two electrons) and anti-bonding (one electron) molecular orbitals. But the Xe electrons would probably lose more energy on leaving the Xe than they would gain by being delocalized to the Li. A different class of molecules could perhaps be formed with highly electropositive atoms involving delocalization of this atom’s electron into the unfilled and highly screened ($n+1$) p -state of the rare gas, for example, LiXe or better the linear XeLi₂. The energy of repulsion of the inner shell electrons would be a determining factor, making LiXe more likely than CsXe despite the differing “electronegativities.”
5. Rotation about the I₂ axis will be possible and one will, therefore, not have separable geometrical conformers. One would expect the propeller-shaped conformer to be the lower energy form and O₂ClF₃ might be just such a molecule built on O₂. The molecule isomeric to *IIIb* with all four F’s on a single I should also exist.
6. Ions are so radically different from molecules—witness the rare gas ions—that they are not considered here. An example of an ion—not a molecule—not involving an “electronegative” atom is He⁺, and an example with extreme geometrical difficulty of approach is CH₅⁺.

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