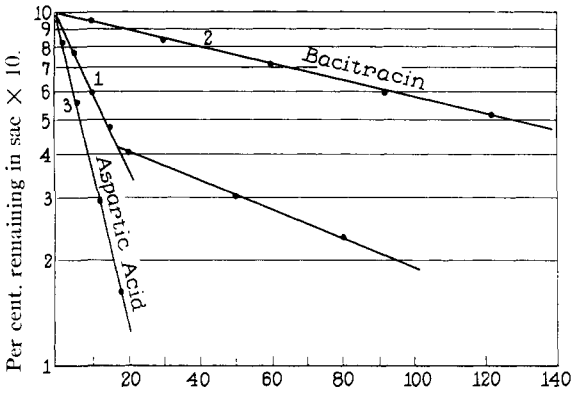

Fig. 2.

different membranes prepared from the same roll appear remarkably reproducible. The most permeable one thus far studied (No. 20/32 "Dialysis tubing")[3] has been found to pass insulin, ribonuclease, lysozyme and chymotrypsinogen in 0.1 *N* acetic acid at characteristically different rates (50% escape times in same cell are 1.6, 3.5, 3.5 and 5 hr., respectively). The membrane permeability can be increased by mechanical stretching so that ovalbumin readily passes.

A full account of this work will be reported soon.

(3) Light and Simpson, *Biochem. Biophys. Acta*, **20**, 251 (1956), found the 20/32 size to pass insulin.

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THE STRUCTURE OF OXIMES

Sir:

Pitt,[1] in a review article, has suggested that oximes should be represented as $R_2C{=}{}^{+}NH{-}O^{-}$ rather than, as ordinarily written, $R_2C{=}N{-}OH$. However, the weight of more recent evidence, set forth below, favors the classical formulation of $R_2C{=}N{-}OH$. The basis for Pitt's suggestion was a preliminary report of the crystal structure determination of *syn-p*-chlorobenzaldoxime.[2] The hydrogen bonding in this crystal was said to be: N. . .O distances of 2.82 Å., with the angles: O–N . . .O′ = 101.4° and N–O. . .N′ = 82°. Since the former is closer to that expected for a covalent bond angle (the hydrogen atom is assumed to lie on or near the N. . .O′ and O. . .N′ axes), the structure $R_2C{=}{}^{+}NH{-}O^{-}$ is indicated. The final results of this structure determination have not yet been published. Dunitz and Robertson[3] later discussed Pitt's suggestion, pointing out that the structure found for acetoxime,[4] with angles O–N. . .O′ of 124° and N–O. . .N′ of 111°, was compatible with either structure, but the results in the case of dimethylglyoxime[5] probably supported Pitt's suggestion. As pointed out by Dunitz and Robertson,[3] Merritt and Lanterman's dimethylglyoxime paper contains an obvious error, since the latter authors stated that both of the above angles equal 75.9°, an impossible situation since the two oxime groups are related by a center of symmetry; Dunitz and Robertson then assumed, apparently by inspection of the published projection of the structure on (001), that the angle N–O. . .N′ was smaller and equal to 75.9°, and that the angle O–N. . .O′ was its supplement, and therefore closer to that expected for the covalent bond. Unfortunately, there is yet another error, for the published parameters give instead for these angles 85° for N–O. . .N′ and 95° for O–N. . .O′, and these are close enough together to cause the argument to lose considerable force.

Additional information relative to this question has appeared recently, namely, the results of the crystal structure of formamidoxime.[6] For this molecule the situation is somewhat more complicated because there are more than just the two tautomeric structures possible. Nevertheless, detailed considerations show that the hydrogen bonding in this crystal is consistent with only two structures, I: $NH_2{-}CH{=}N{-}OH$, and II: $^{-}NH{-}CH{=}N{-}{}^{+}OH_2$. (Each of these has more than one resonance form.) The structure $NH_2{-}CH{=}{}^{+}NH{-}O^{-}$ is in particular eliminated because both atoms which form hydrogen bonds with the oxime nitrogen atom lie so far from the molecular plane that this atom must be the acceptor atom in these two hydrogen bonds. Structure II above, may be rejected[6] on the ground that the relative electronegativities of oxygen and nitrogen will render both of its resonance forms unstable. We are thus left with Structure I, and the observed bond lengths indicate that the formamidoxime molecule is best represented as a resonance hybrid, the predominant forms being $NH_2{-}CH{=}N{-}OH$ and $^{+}NH_2{=}CH{-}N^{-}{-}OH$, which contribute about equally, and perhaps a small contribution of the form $NH_2{-}{}^{-}CH{-}N{=}{}^{+}OH$.

At present, therefore, it appears that the usual oxime structure, $R_2C{=}N{-}OH$, is correct, but obviously a direct location of the hydrogen atoms in an oxime by use of accurate three dimensional X-ray data, or by neutron diffraction, would be highly desirable.

(1) G. J. Pitt, *Annual Reports of the Chemical Society*, **47**, 457 (1950).
(2) B. Jerslev, *Nature*, **166**, 741 (1950).
(3) J. D. Dunitz and J. H. Robertson, *Annual Reports of the Chemical Society*, **49**, 378 (1952).
(4) T. K. Bierlien and E. C. Lingafelter, *Acta Cryst.*, **4**, 450 (1951).
(5) L. L. Merritt and E. Lanterman, *ibid.*, **5**, 811 (1952).
(6) D. Hall and F. J. Llewellyn, *ibid.*, **9**, 108 (1956).

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THE STRUCTURES OF SINIGRIN AND SINALBIN; AN ENZYMATIC REARRANGEMENT

Sir:

The myronate ion, isolated as the potassium salt sinigrin in 1839, is the precursor of the isothiocyanate of black mustard and horseradish and the prototype of mustard oil glucosides. The currently accepted structure (I, R = $H_2C{=}CHCH_2$), proposed in 1897,[1] rested on the enzymatic hydrolysis of sinigrin to allyl isothiocyanate, D-glucose and bisulfate ion, the cleavage by silver nitrate to glucose and silver sinigrate, $C_4H_5O_4NS_2Ag_2$, a mer-

(1) J. Gadamer, *Arch. Pharm.*, **235**, 44 (1897).