

which both hydroxyl groups are primary, is favored by the ready formation of a ditrityl derivative.

Evidence which served to distinguish unambiguously among the above structures was provided by the following sequence of reactions: (i) Treatment of serratamolide with methanesulfonyl chloride in pyridine gave the unstable dimethanesulfonyl derivative, m.p. 125–127° (dec.), which was converted rapidly with lithium bromide in methyl ethyl ketone to the neutral dibromo derivative, m.p. 170° (dec.). Calcd. for $C_{26}H_{44}O_6N_2Br_2$: C, 48.76; H, 6.92; N, 4.37; Br, 24.96. Found: C, 49.13; H, 6.75; N, 4.48; Br, 24.40. (ii) Hydrogenation of the dibromo derivative⁷ (Pd/methanol/NaOH) yielded a debrominated product (not isolated) which was immediately hydrolyzed with concd. HCl, producing a mixture of acids. As a result of these changes ($-OH \rightarrow -O-Mesyl \rightarrow -Br \rightarrow -H$), II would yield alanine and 3-hydroxydecanoic acid, III would yield serine and decanoic acid, while IV would give rise to all four of the above acids.

Examination of the aqueous acidic hydrolyzate by both paper chromatography and ion-exchange chromatography⁸ showed alanine (67%) as the only amino acid present in more than trace amounts. A control hydrolysis of serratamolide under the same conditions gave serine in 92% yield. The other acidic product of the sequence outlined in (i) and (ii) above, obtained by ether extraction of the hydrolysate, was methylated with diazomethane and was shown by vapor phase chromatography to be the methyl ester of 3-hydroxydecanoic acid. No peak corresponding to methyl decanoate was detected.

(7) Cf. reduction of chloroserratamic acid to deoxyserratamic acid, N. J. Cartwright, *Biochem. J.*, **67**, 668 (1957).

Structure II is thus unique in accommodating all of the properties of serratamolide, which differs from the depsipeptides⁸ such as valinonycin and the enniatins in that it contains β -hydroxy acid, rather than α -hydroxy acid residues.

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(8) See the review of depsipeptides by M. M. Schemjakin, *Angew. Chem.*, **72**, 342 (1960).

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RECEIVED AUGUST 18, 1961

OXAZAHYDROBORATE IONS

Sir:

We wish to report the preparation of three members of a new class of hydroborate ions which apparently contain the oxaza (NO) group. These anions were obtained by the reaction of nitrogen dioxide with the perhydrodecaborate ($B_{10}H_{10}^{-2}$) ion,^{1,2} or by the reaction of this ion with nitric oxide in the presence of ferric ion. These conditions suggest that an oxidation-reduction reaction is involved. Molecular weights and magnetic properties have not been determined as yet and thus only the simplest empirical formulas are reported.

Addition of 0.010 mole NO_2 in 100 ml. of methylene chloride to a solution of 0.010 mole of triethylammonium perhydrodecaborate in 100 ml. of 10% aqueous acetonitrile at 0° produced a dark blue solution from which $B_{11}H_{12}NO(NH_2Et_3)_2$ was isolated in 60–65% yield, as purple crystals.

Anal. Calcd. for $C_{12}H_{44}B_{14}N_3O$: C, 36.21; H, 11.14; B, 38.06; N, 10.56. Found: C, 36.26; H, 11.36; B, 37.36; N, 10.46.

The compound also could be obtained when ferric ion and nitric oxide were employed instead of nitrogen dioxide. However, the presence of by-products made the purification more difficult. The oxaza group readily was reduced by Raney nickel-catalyzed hydrogenation to the corresponding amino hydroborate salt, $B_{14}H_{13}NH_2(NH_2Et_3)_2$. Its infrared spectrum showed N–H stretch (2.80μ) and deformation (6.42μ) in addition to the $-NH$ stretch of the cation (3.22μ).

Anal. Calcd. for $C_{12}H_{47}B_{14}N_3$: C, 37.43; H, 12.30; B, 39.34; N, 10.91. Found: C, 37.51; H, 11.96; B, 39.30; N, 10.30.

Two other oxazahydroborate ions were formed when gaseous nitrogen dioxide was introduced into a 10% aqueous acetonitrile solution of perhydrodecaborate ion. In this case compounds were obtained which contained more than one NO group per hydroborate ion. These materials were red crystalline solids which had compositions $[B_{10}H_8(NO)_2 \cdot N(CH_3)_4]$ (calcd.: C, 20.67; H, 7.80; B, 46.56; N, 18.08. Found: C, 20.38; H, 7.61; B, 46.27; N, 17.93) and $[B_{10}H_4(NO)_3 \cdot N(CH_3)_4]$ (calcd.: C, 17.38; H, 5.83; B, 39.14;

(1) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(2) W. N. Lipscomb, A. R. Pitochelli and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

N, 20.27. Found: C, 17.42; H, 5.98; B, 38.87; N, 19.91). The latter was quite impact sensitive. The exact empirical formulas, with respect to hydrogen, are not known. A Raney nickel-catalyzed hydrogenation of the above two oxazabodborate salts removed oxygen from the materials. The infrared spectra of the new products suggest that no N-H linkages are present, in contrast to the reduction product of $B_{14}H_{12}NO^{-2}$. Further characterization of these materials is in process.

Anal. [$B_{10}H_8N_2 \cdot N(CH_3)_4$]: calcd.: C, 21.89; H, 9.65; B, 49.30; N, 19.15. Found: C, 21.62; H, 9.54; B, 50.01; N, 19.24. [$B_{20}H_8N_3 \cdot N(CH_3)_4$]: calcd.: C, 20.67; H, 8.67; B, 46.55; N, 24.10. Found: C, 19.96; H, 8.42; B, 47.02; N, 23.91.

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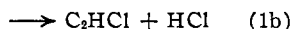
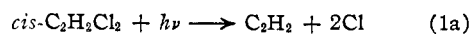
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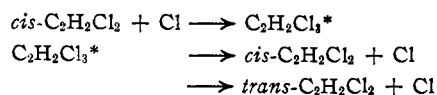
MOLECULAR DETACHMENT OF HYDROGEN CHLORIDE IN THE PHOTOLYSIS OF CIS-1,2-DICHLOROETHYLENE¹

Sir:

Recently^{2,3} data have been published on molecular detachment processes in the vacuum ultraviolet photolysis of gaseous hydrocarbons. We have now obtained evidence that the molecular detachment of hydrogen chloride may be important in photochemical decompositions of chlorine containing compounds. Photolysis of *cis*-1,2-dichloroethylene indicates that these primary processes occur



The evidence for steps 1a and 1b is based upon the following facts. The rates of formation of C_2H_2 and C_2HCl are directly proportional to the incident light intensity. This indicates that these products are not formed by free radical disproportionation reactions. The rates of formation of C_2H_2 and C_2HCl are not reduced by the addition of isobutylene and of iodine as free radical scavengers. On the other hand, free radical reactions, such as the formation of *trans*-1,2-dichloroethylene, are severely reduced by the addition of free radical scavengers. *trans*-1,2-Dichloroethylene is produced to a large extent by the reactions.



Photochemical experiments using the full light of the Hanovia medium pressure arc (Type 16 A 13) yield a value of about 9 for the ratio C_2H_2/C_2HCl .

(1) This investigation was supported, in part, by the U. S. Atomic Energy Commission.

(2) H. Okabe and J. R. McNesby, *J. Chem. Phys.*, **34**, 668 (1961).

(3) L. M. Dorfman and M. C. Sauer, Jr., presented at the 139th National Meeting of the American Chemical Society at St. Louis, Mo., 1961.

This ratio is reduced to about 3.3 if the light is transmitted through Corning filter No. 9-54 (transmitting above 2200 Å). This indicates that C_2H_2 and C_2HCl originate from different electronic excitation levels. Since primary step 1a undoubtedly is more endothermic than step 1b it would be expected that lower wave lengths favor step 1a over step 1b as observed. In determining the ratio C_2H_2/C_2HCl by gas chromatography we have assumed that C_2HCl and C_2H_3Cl have the same sensitivity. This is an approximation and most likely the actual values for C_2H_2/C_2HCl will be somewhat lower than reported here. Further confirmation for steps 1a and 1b was obtained from mass spectrometer data which indicate that in the presence of free radical scavengers HCl but not Cl_2 is produced. This is in agreement with observations by Mahncke and Noyes.⁴ These authors observed the production of HCl in the photolysis of *cis*- $C_2H_2Cl_2$ but did not obtain positive evidence for the production of Cl_2 .

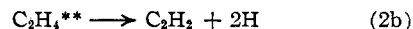
It is possible that primary step 1a may occur in two steps as suggested by Futrell and Newton⁵ in the liquid phase radiolysis of symmetrical dichloroethylenes



At the present time it is not possible to discriminate between this process and the simultaneous ejection of two chlorine atoms when the acetylene bond is formed as indicated by step 1a.

Our data show a great similarity between radiation chemistry data and conventional photochemical data. The radiolysis of symmetrical dichloroethylenes in the liquid phase has been studied by Futrell and Newton.⁵ They observed C_2H_2 , C_2HCl and HCl as the major volatile products and explain their formation by steps 1b, 1c and 1d. Similar results have been obtained for the γ -ray radiolysis of gaseous *cis*- $C_2H_2Cl_2$ where $G_{C_2H_2}$ and G_{C_2HCl} were found to be independent of the presence or absence of free radical scavengers.⁶

It is also clear that steps 1a and 1b are similar to steps 2a and 2b



which have been shown to occur in the vacuum ultraviolet photolysis of ethylene³ and which steps most likely play a major role in the radiolysis of ethylene.

At this time we have no information *pro* or *con* regarding possible primary step 1e, suggested by Mahncke and Noyes.⁴



We expect that further investigations will yield information regarding step 1e. We are

(4) H. B. Mahncke and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **55**, 932 (1933).

(5) J. H. Futrell and A. S. Newton, *ibid.*, **82**, 2676 (1960).

(6) M. H. J. Wijnen, to be published.