

- in the  $t\text{-C}_4\text{H}_9\text{CCl}$  reaction.
- (24) For reviews of the structures of the isoelectronic cyclopropylcarbonyl cations, see (a) H. G. Richey, Jr., in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, 1972, pp 1216 ff; and (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe., III, ref 24a, pp 1295 ff.
- (25) Facile 1,2-hydride migrations are generally believed to require a near  $-0^\circ$  dihedral angle between the carbenic p orbital and the adjacent C-H bond: A. Nickon, F.-c. Huang, R. Weglein, K. Matsuo, and H. Yagi, *J. Am. Chem. Soc.*, **96**, 5264 (1974). See, however, E. P. Kyba and C. W. Hudson, *ibid.*, **98**, 5696 (1976); E. P. Kyba and A. M. John, *ibid.*, **99**, 8329 (1977); and E. P. Kyba, *ibid.*, **99**, 8330 (1977).
- (26)  $\pi$ -p donation from a phenyl substituent to the carbenic center is apparently less effective; cyclopropylphenylcarbene, in contrast to 1, rearranges to 1-phenylcyclobutene more rapidly than it can be trapped with alkenes: P. C. Petrellis, G. W. Griffin, M. E. Hendrick, and M. Jones, Jr., *J. Chem. Soc., Chem. Commun.*, 1002 (1972).

Robert A. Moss,\* Mary E. Fantina

Wright and Rieman Laboratories, Department of Chemistry  
Rutgers, The State University of New Jersey  
New Brunswick, New Jersey 08903

Received June 9, 1978

## "Water Splitting" by Titanium Exchanged Zeolite A

Sir:

Nonpolluting, hydrogen burning automobile engines<sup>1</sup> provide one of many practical motivations for seeking cheaper hydrogen. The possibility that solar illuminated inorganic complexes economically effect "water splitting" has inspired reviews<sup>2-4</sup> and experiments.<sup>5-9</sup> One subscheme<sup>10,11</sup> involves visible illumination of transition metal ion exchanged zeolites. Production of oxygen or hydrogen by such exchanged zeolites immersed in water and exposed to visible light can be demonstrated, but economical restoration of the transition metal in the zeolite to the oxidation state required for repetition of the gas production step is difficult. We have investigated properties of titanium(III) exchanged zeolite A (Linde 3A) which when bathed in water under visible illumination yields hydrogen.

Titanium(III) exchanged zeolite A is difficult to prepare using aqueous titanous chloride solution (Fisher Scientific Co. 20%, pH  $\sim$ 0).  $\text{TiCl}_3$  (aqueous) is unstable in nonacidic media (precipitating as  $\text{Ti}(\text{OH})_3$ ), whereas zeolite A is unstable under acidic conditions. In a conventional ion exchange procedure wherein solution and zeolite are combined in proportions of 1 L:  $\sim$ 20 g, stirring several days produces an amorphous gel. This may be circumvented by a high zeolite to solution ratio that capitalizes on a buffering capacity of the zeolite 3A (unit cell composition:<sup>12</sup>  $\text{K}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ). ESCA (Hewlett-Packard Model 5950B) peak areas indicate that 75% of the potassium cations is replaced by titanium cations on the surface of  $1/16$ -in.-diameter Linde 3A extrudate by letting 25 g of zeolite A stand in 50 mL of unstirred 20%  $\text{TiCl}_3$  solution for an hour at ambient temperature. The cages probably remain intact under these conditions since little aluminum leaching ( $\sim$ 25%) is indicated by the ESCA profile of the top  $\sim$ 50 Å of these pellets. Absence of chlorine in the ESCA spectrum indicates that titanium cations exchange into the zeolite rather than merely occlude as titanous chloride from solution. When this now-purple (characteristic color of hexaquotitanium(III) ions) exchanged zeolite is washed with deionized water under air until no further  $\text{TiCl}_3$  is eluted and is then illuminated with visible light (of any wavelength including red), gas bubbles form after an induction period of a minute or less. (The action spectrum may be determinable by photoacoustic spectroscopy.<sup>13</sup>) The reaction can be repeatedly started and stopped by exposure to weak illumination ( $\leq$  80 ft-c). Direct exposure to strong illumination ( $\geq$  8000 ft-c) for  $>$  5 min causes gas evolution for  $\sim$ 45 min without continued illumination, resulting

in the production of  $\sim$ 0.4 mL/g extrudate. The gas is 40% hydrogen by chromatographic analysis,<sup>14</sup> the remainder being  $\text{O}_2$  and  $\text{N}_2$  in the normal air ratio. Mass spectrometry confirms the presence of significant amounts of hydrogen. Titanium exchanged zeolites X and Y do not evolve detectable  $\text{H}_2$  under the above conditions.

Titanium(III) in zeolite A has an ESR spectrum (Varian E-3 EPR spectrometer) virtually identical with that observed by Ono et al.<sup>15</sup> for titanium(III) in zeolite Y. The line width in both cases is  $\sim$ 35 Oe with an isotropic peak confirmed in the present work to have a  $g = 1.950$  in Y-type zeolites and centered at 1.952 in the A type. Such a sample of vacuum-dehydrated titanium(III) in zeolite A exposed to oxygen in a light-tight ESR tube (i.d. 5 mm) retains the full intensity of the ESR signal just described. This contrasts with the observation of Ono et al.<sup>15</sup> and our own finding that a peroxide (denoted as  $\text{Ti-O-O}^-$ ) forms in Y-type zeolites exposed to oxygen. Illumination of the oxygen exposed zeolite A produces an intense, isotropic ESR signal at  $g = 2.0090$  with a line width of 7 Oe. This latter spectrum we attribute to a titanium(IV)-oxygen complex in which four oxygen atoms surround the titanium atom in a perfect tetrahedron with the unpaired electron shared equally by the oxygen atoms. ESCA data support the  $\text{TiO}_4$  stoichiometry. If the material is dehydrated ("activated") under vacuum at 200 °C, the radical persists indefinitely. However, admission of moisture promptly produces hydrogen gas and concomitant loss of the ESR signal with the rate of loss proportional to the amount of water (vapor or liquid) admitted. Thus it is this photoformed radical which is the precursor of  $\text{H}_2$  formation in water submerged titanium-zeolite A. An analogous sequence of procedures using  $\text{SO}_2$  in lieu of  $\text{O}_2$  produces an identical ESR spectrum with noticeable yellowing of the material, presumably caused by elemental sulfur formation. In this case, the free radical again disappears with gas bubbling on admission of moisture.

Cations in zeolites may be thermally restored to an oxidation state that gives rise to either thermolysis or photolysis of water.<sup>10,11,16</sup> Thermolysis has been demonstrated for chromium and indium in Y zeolites,<sup>16</sup> whereas photolysis has been observed in silver exchanged Y- and A-type zeolites.<sup>10,11</sup> In the present case of titanium exchanged zeolite A the radical oxygenated complex may be thermally regenerated (275 °C at  $3 \times 10^{-2}$  Torr) yielding an ESR signal over half as large after 4 h as the initial intensity. Oxygen could conceivably evolve during the thermolysis but is not detectable chromatographically (since the process occurs under vacuum.) Heating above 400 °C, rather than regenerating more of the desired free radical, produces an unidentified radical species with an anisotropic peak centered at  $g = 1.974$ .

Thus a means other than heating must be found to achieve a closed photochemical cycle that harnesses visible solar energy in the production of molecular hydrogen. The titanium exchanged zeolite A does, however, lend itself to a thermolysis of water described previously.<sup>16</sup>

**Acknowledgment.** Financial support from the Office of Naval Research and the Department of Energy and Professor K. L. DeVries' generous help with his ESR spectrometer are gratefully acknowledged.

**Supplementary Material Available:** ESCA spectra and discussion (20 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) In one hydrogen fueled automotive engine (Billings Corp., Provo, Utah) 0.79 kg of  $\text{H}_2$  is equivalent to 1.0 gal of gasoline. Electrolysis units sold with these engines consume 131 kWh of electrical power per kilogram of  $\text{H}_2$  produced. Even neglecting capital costs of electrolysis units and  $\text{H}_2$  storage tanks,  $\text{H}_2$  is thus an economically disadvantageous fuel at prevailing prices of electricity and gasoline by a factor of  $\sim$ 7.

(2) R. J. Marcus, *Science*, **123**, 399 (1965).  
 (3) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and M. Gleria, *Science*, **189**, 852 (1975).  
 (4) D. D. Davis, G. K. King, K. S. Stevenson, E. R. Birnbaum, and J. H. Hageman, *J. Solid State Chem.*, **22**, 63 (1977).  
 (5) C. Creutz and N. Sutin, *Proc. Natl. Acad. U.S.A.*, **72**, 2858 (1975).  
 (6) G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 2337 (1976); **99**, 4947 (1977).  
 (7) K. R. Mann, N. S. Lewis, V. M. Miskowski, D. K. Erwin, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **99**, 5525 (1977).  
 (8) J.-M. Lehn and J.-P. Sauvage, *Nouv. J. Chim.*, **1**, 449 (1977).  
 (9) F. K. Fong and L. Galloway, *J. Am. Chem. Soc.*, **100**, 3594 (1978).  
 (10) S. Leutwyler and E. Schumacher, *Chimia*, **31**, 475 (1977).  
 (11) P. A. Jacobs, J. B. Uytterhoeven, and H. K. Beyer, *J. Chem. Soc., Chem. Commun.*, 128 (1977).  
 (12) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).  
 (13) R. C. Gray and A. J. Bard, *Anal. Chem.*, **50**, 1262 (1978).  
 (14) S. J. Valenty, *Anal. Chem.*, **50**, 669 (1978).  
 (15) Y. Ono, K. Suzuki, and T. Keii, *J. Phys. Chem.*, **78**, 218 (1974).  
 (16) P. H. Kasai and R. J. Bishop, Jr., *J. Phys. Chem.*, **81**, 1527 (1977); see also U.S. Patent 3 963 830 (June 15, 1976).

Steven M. Kuznicki, Edward M. Eyring\*  
 Department of Chemistry, University of Utah  
 Salt Lake City, Utah 84112  
 Received June 26, 1978

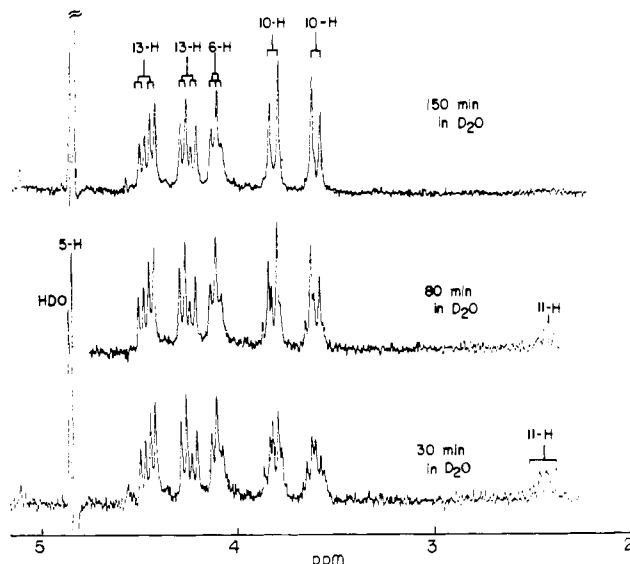


Figure 1. <sup>1</sup>H NMR of neosaxitoxin (**1**) (~1 mg) in D<sub>2</sub>O after 30 min, 80 min, and 2.5 h. The strong water band around 4.8 ppm was largely removed by the PRFT technique in order to observe the H-5 signal. All <sup>1</sup>H NMR spectra showed a strong peak at ~2.0 ppm due to the acetate counterions.

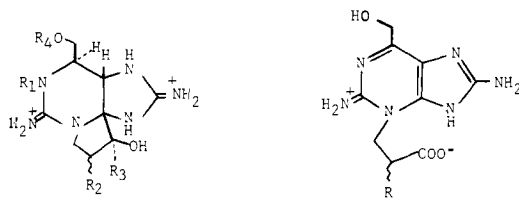
Structure of Neosaxitoxin

Sir:

Neosaxitoxin was first isolated as a minor toxin constituent in the toxic Alaska butter clam, *Saxidomus giganteus*, and later as a major toxin in the cultured dinoflagellate, *Gonyaulax tamarensis*, which causes the North Atlantic paralytic shellfish poisoning (PSP).<sup>1</sup> It has since been isolated from a number of organisms: the toxic mussel, *Mytilus edulis*, from Haines, Alaska;<sup>2</sup> the sea scallop, *Placopecten magellanicus*, from the Bay of Fundy, Canada;<sup>3</sup> and several other unidentified *Gonyaulax* species.<sup>4</sup>

This toxin is of particular interest because, although it is a major toxin in *G. tamarensis*, only trace amounts of it were found in the soft-shell clam, *Mya arenaria*, infested by the dinoflagellate. The major toxin of *Mya arenaria* was found to be saxitoxin, and hence a biotransformation of neosaxitoxin to saxitoxin by the shellfish is suggested.

Neosaxitoxin (**1**) is very similar to saxitoxin (**2**) in its



- 1 R<sub>1</sub>, R<sub>3</sub> = OH; R<sub>2</sub> = H; R<sub>4</sub> = -CONH<sub>2</sub>
- 2 R<sub>1</sub>, R<sub>2</sub> = H; R<sub>3</sub> = OH; R<sub>4</sub> = -CONH<sub>2</sub>
- 3 R<sub>1</sub> = H; R<sub>2</sub> = α-OH; R<sub>3</sub> = OH; R<sub>4</sub> = -CONH<sub>2</sub>
- 4 R<sub>1</sub> = H; R<sub>2</sub> = β-OH; R<sub>3</sub> = OH; R<sub>4</sub> = -CONH<sub>2</sub>
- 7 R<sub>1</sub>, R<sub>2</sub>, R<sub>4</sub> = H; R<sub>3</sub> = OH
- 8 R<sub>1</sub>, R<sub>3</sub> = OH; R<sub>2</sub>, R<sub>4</sub> = H
- 11 R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> = H; R<sub>4</sub> = -CONH<sub>2</sub>

chromatographic behavior and is only separable from the latter by careful gradient ion-exchange chromatography.<sup>1</sup> Its toxicity is comparable with that of saxitoxin (5000 mouse units/mg ± 500); the infrared spectrum is also very similar except for a slightly pronounced shoulder in the carbonyl region (1770 cm<sup>-1</sup>).<sup>1</sup> The molecular formula could not be obtained directly because of its highly hygroscopic, amorphous, and nonvolatile nature. The following structural studies were carried out on

a total of 2 mg of the toxin which was obtained from cultures of *G. tamarensis*.<sup>1</sup>

The structures of saxitoxin (**2**)<sup>5,6</sup> and two other PSP toxins, gonyautoxins II (**3**) and III (**4**),<sup>7</sup> have recently been established. Saxitoxin (**2**) and gonyautoxin II (**3**) gave the aromatized aminopurinypropionic acid derivatives **5** and **6**, respectively, by oxidation with H<sub>2</sub>O<sub>2</sub>-NaOH.<sup>7-9</sup> The oxidation products **5** and **6** are highly fluorescent and have characteristic UV absorptions with λ<sub>max</sub> of 335 and 337 nm, respectively. When neosaxitoxin (**1**) was oxidized under the same condition, however, no UV-absorbing product was obtained; it was only upon H<sub>2</sub>O<sub>2</sub> oxidation in neutral aqueous medium that **1** gave a minute amount of a fluorescent product with UV absorption (λ<sub>max</sub> 335 nm) corresponding to that of **5**. This result suggests the presence of the same nucleus in neosaxitoxin (**1**) as in saxitoxin (**2**) and gonyautoxin II (**3**).

The 220-MHz partially relaxed Fourier transform (PRFT) <sup>1</sup>H NMR of **1** in D<sub>2</sub>O (Figure 1)<sup>10</sup> showed again a close resemblance to that of saxitoxin (**2**). It was noted that the ~2.44-ppm 11-H multiplet was rapidly deuterated and disappeared in about an hour, and that two multiplets centered at 3.80 and 3.58 ppm (10-H's) were converted into a well-defined AB-type quartet. This phenomenon corresponds to the known deuterium exchange of 11-H<sub>2</sub> of saxitoxin (**2**).<sup>11</sup> However, in **2** this exchange through enolization takes place at the much slower rate of over a period of 2 weeks. The rapid deuterium exchange in **1** is also noticeable in the <sup>13</sup>C NMR spectrum where the C-11 appeared only as a weak signal owing to the two deuterium attachment.<sup>12</sup> The <sup>13</sup>C NMR spectrum in D<sub>2</sub>O showed only two signals in the sp<sup>2</sup> carbon region which first led us to suspect that **1** might be a decarbamoyl derivative of saxitoxin. However, direct comparison of **1** with decarbamoylsaxitoxin (**7**)<sup>13</sup> clearly ruled out this possibility. Namely, when **1** was treated with 7.5 N HCl, a condition to effect hydrolysis of the carbamoyl group,<sup>13</sup> a new product, **8**, which maintains ~70% of the original toxicity, was isolated.<sup>1</sup> This observation closely parallels that of saxitoxin suggesting presence of the carbamoyl moiety in **1**. This problem was finally resolved with the detection of three peaks at 157.4, 158.5, and 159.0 ppm in C<sub>5</sub>D<sub>5</sub>N containing a trace of D<sub>2</sub>O.

The proton and carbon chemical shifts of neosaxitoxin (**1**) and saxitoxin (**2**) are summarized in structures **9** and **10** (Chart I). The closeness of <sup>1</sup>H NMR coupling patterns of **1** and **2**