ratios are not seen. We are left with the conclusion that the compounds under discussion display intense correlation-state structures on the N 1s ionizations, a unique behavior, to our knowledge.

It is difficult to provide an incisive discussion of the correlation-state structures we observe without having calculations on the electronic structures of at least some of the molecules at hand. Magnesium porphyrin has been discussed in some detail by Maggiora and co-workers.[14,15] According to these calculations, all the molecular orbitals within several electronvolts on either side of the highest occupied orbital of magnesium porphyrin are of porphyrin π type, containing essentially no Mg $3p_z$ contribution. It is most likely, thus, that any low-lying excited states of the core-ionized species would derive from excitation from a filled π orbital to an empty π orbital. The calculations furthermore show that the π system of magnesium porphyrin has little electron density on Mg. Thus, the Mg $3p_z$ orbital is essentially decoupled from the porphyrin in the ground state and lower excited states of magnesium porphyrin.

The results outlined in the last paragraph leave only one role for the Mg in promoting the appearance of low-lying correlation-state structure: the strong perturbation which comes from core ionization of a nitrogen atom causes Mg $3p_z$ amplitude to be mixed into the upper filled and lower virtual orbitals of the core-hole state as part of the electronic rearrangement of the system. Magnesium $3p_z$ amplitude can appear in many of the core-hole state π orbitals (to be precise, those arising from a_1, a_2, or e orbitals of magnesium porphyrin) because the perturbation breaks the symmetry of the system. Satellites then arise because the various final states must be superimposed so as to give the original electronic structure.

The extension of the arguments applied to magnesium porphyrin to other compounds is rather difficult because many virtual levels are available and may be mixed into the electronic structure by the perturbation caused by photoionization. Thus, further discussion of the other systems must await the appearance of more calculational data.

Acknowledgments. The support of this work by NIH under Grant HL-13651 is acknowledged gratefully. We are grateful to Professor M. Gouterman, who very kindly allowed us to examine his lanthanide porphyrins.

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Dogger Bank Itch. The Allergen Is (2-Hydroxyethyl)dimethylsulfonium Ion

Sir:

We report the isolation, structure elucidation, and synthesis of the causative agent of Dogger Bank itch,[1,2] an eczematous allergic contact dermatitis caused by exposure to the marine bryozoan, *Alcyonidium gelatinosum* (L.).[3-6] These marine animals[7] were kept and reextracted with ethanol (96%) to give an inactive residue and active extracts as demonstrated by patch tests on sensitized volunteers,[8] a bioassay which has been used all through the isolation procedure. Evaporation of the combined extracts followed by partition between water and ether proved the activity to be entirely concentrated in the aqueous phase. Sephadex G-10 gel chromatography with water as eluant gave rise to a salt fraction (~0.7% C) displaying almost the entire activity.

In order to reduce the amount of salt, the active gel filtration fraction was extracted with absolute ethanol after freeze-drying. The supernatant held most of the activity and left, on evaporation, a sample which was subjected to repeated ion-exchange chromatography (Dowex 50W-X8). Still the allergen appeared associated with the salt fraction after elution with hydrochloric acid. The carbon content had, however, risen to 7% and cutaneous patch tests revealed an exceedingly high activity. Noise-decoupled 67.889-MHz ^{13}C NMR in D_2O virtually only exhibited three signals at δ 42.3, 56.0, and 57.5 ppm. These signals could be traced back in the earlier active fractions. The signals appeared with integrals roughly 2:1:1, respectively, and with off-resonance decoupling identified themselves as belonging to methyl groups and two magnetically different methylene groups, respectively. The same solution subjected to 270-MHz ^{1}H NMR gave rise to signals at δ 3.9 (br s) and 4.3 (br s) ppm integrating in the ratio 3:2.[9] Elemental analyses of this fraction (lyophilized) gave a C to S ratio of 0.6617 as compared to a calculated value of 0.6668 for $C_4H_{11}O_2S$. High-resolution electron-impact mass spectrometry at 200 °C only gave substantial fragments at *m/e* 78.0145 (C_2H_6OS, calcd 78.0139) and 62.9951 (CH_3OS, calcd 62.9904). Loss of a methyl group from *m/e* 78 producing *m/e* 63 was substantiated by a metastable peak at *m/e* 50.88. This spectrum was identical with a spectrum of dimethyl sulfoxide.

For comparative purposes the ^{13}C and ^{1}H NMR spectra of sulfocholine[10] ((2-hydroxyethyl)dimethylsulfonium ion) were recorded. In this case the methyl group signals were found at δ 27.7 and 2.96 (s) ppm, the methylene group adjacent to sulfur at δ 48.7 and 3.55 (m), and the methylene group bearing the hydroxyl at δ 58.2 and 4.13 (m) ppm. Clearly the allergen bears a group more deshielding than the sulfonium entity. After this was taken into account, the spectra of the trimethylsulfoxonium ion[11] were recorded, the methyl groups appearing at δ 42.3 and 3.93 in the ^{13}C and ^{1}H NMR spectra, respectively.

From the above-mentioned data it is concluded that the Dogger Bank itch producing allergen must be (2-hydroxyethyl)dimethylsulfoxonium ion. This structure assignment was further substantiated by field desorption (FD) MS measurements. At 80 °C ion source temperature, three significant ions were observed at *m/e* 108 (25%), 90 (25%), and 78 (100%), assigned to the molecular ions of methyl (2-hydroxyethyl) sulfoxide, methyl vinyl sulfoxide and dimethyl sulfoxide respectively, which were thought to be formed thermally from the allergen precursor. At 200 °C the pattern was *m/e* 108 (15%), 90 (30%), and 78 (100%). As expected, the EI–MS at the latter temperature was more complicated, *m/e* 90 (3%), 78 (88%), 63 (100%), 61 (17%), and 50 (95%)/52 (30%), representing methylchloride molecular ion. The structure of one of the key ions, *m/e* 90, was strongly supported

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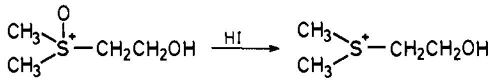
by an EI (70 eV–100 μA, 200 °C) collision induced decomposition[12] (CID, He, $p \sim 10^{-4}$ mmHg) experiment producing a CID mass spectrum identical with a computer-stored spectrum of the authentic compound. The observed behavior of the allergen in FD MS closely parallels that of the model compound trimethylsulfoxonium iodide giving rise to m/e 142 (CH_3I^+), 93 ($(CCH_3)_3S^+O$), and 78 (Me_2SO^+) at 80 °C.

Finally, strong support for the proposed structure was gained from hydrogen iodide reduction (67% HI, reflux for 15 min) of the active salt fraction, leaving sulfocholine in analogy with the recorded reduction of trimethylsulfoxonium ion to trimethylsulfonium ion.[11]



The pure allergen (estimated 5 ppm based on animal wet weight) could be isolated from the salt mixture by precipitation of an iodo complex from an acidic (1 N H_2SO_4) solution containing the triiodo ion.[13] In analogy with quaternary ammonium ions, a precipitate is formed.

Synthesis of the allergen has been achieved by the base-catalyzed reaction of trimethylsulfoxonium chloride and formaldehyde in aqueous solution at room temperature.[14]

Sulfoxonium ions have never been encountered in nature before and are, except for a very few examples,[15] the most prominent being trimethylsulfoxonium ion, virtually chemically unknown. The chemistry, pharmacology, and natural distribution of this rare type of compound are at present being investigated.

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Continuous-Wave CO_2 Laser-Induced Decomposition of Phosgene in BCl_3: A Thermal Reaction

Sir:

The value of lasers for purifying materials has been demonstrated in several laboratories.[1-4] Of particular interest is the work of Merritt and Robertson[3] and later Bachmann et al.,[4] who showed that low-power continuous-wave (CW) CO_2 laser irradiations could be utilized to selectively dissociate phosgene ($COCl_2$) impurity usually present in BCl_3. While the utility of the phosgene results cannot be disputed, the interpretations presented are open to question.

Merritt and Robertson irradiated BCl_3–$COCl_2$ mixtures having total pressures varying between 12 and 110 torr with a multiline CW CO_2 laser at 100 W. BCl_3 is the predominant absorber under these conditions. They found $COCl_2$ to be decomposed quickly and selectively. On the other hand, simple heating of corresponding samples to 200 °C for several hours resulted in no $COCl_2$ decomposition. Substituting C_2H_4 for BCl_3 also resulted in $COCl_2$ decomposition, but at a reduced rate. Bachmann et al. irradiated their samples with a CW CO_2 laser operating on a single P-24 (944.10 cm^{-1}) line at 6 W. Pressures of their static or flowing $COCl_2$–BCl_3 mixtures were always greater than 100 torr. Again, $COCl_2$ was selectively dissociated. Replacement of BCl_3 with SF_6, which is a stronger absorber than BCl_3, and irradiation with the P-20 (940.52 cm^{-1}) line resulted in significantly less dissociation of $COCl_2$. Both groups interpreted their results in terms of a nonthermal mechanism, namely, energy transfer from vibrationally excited BCl_3 to $COCl_2$. Bachmann et al.[4] also expressed the possibility that a "fragmentation product of BCl_3" could be responsible for the degradation of $COCl_2$, with the fragment originating from direct-laser vibrational–excitational dissociation of the BCl_3 absorber.

However, under the conditions of these experiments, elementary considerations would indicate the results should be a reflection of low photon density and high collision numbers. At most, only 10^3–10^4 photons/s reach the proximity of an absorbing molecule while the same molecule is undergoing approximately 10^8–10^9 collisions/s. Thus, highly vibrationally excited BCl_3 or fragments of BCl,3 produced by direct-laser multiple-photon absorption under these conditions seems improbable. On the other hand, a high-temperature zone within the irradiating beam envelope is produced, and there would be a corresponding molecular vibrational distribution.[5,6]

The present work was carried out to determine if vibrationally excited molecules produced by multiple-photon absorption were involved or if a thermal process was taking place subsequent to vibrational–translational energy transfer from the laser-excited BCl_3. To make this distinction, we carried out on BCl_3–$COCl_2$ mixtures experiments similar to those recently made on neat B_2H_6[7] and B_2H_6–SF_6 mixtures[8] involving chopped and unchopped CW CO_2 laser irradiations.

The samples were prepared from BCl_3 and $COCl_2$ purchased from Matheson and Linde, respectively. Both gases were purified by vacuum distillation, checked by IR, and stored in glass vials fitted with greaseless Teflon stopcocks. The irradiations were carried out in a greaseless 10-cm path length, 140.58-cm^2 glass cell fitted with NaCl windows, Viton O-rings, a Teflon stopcock, and a side arm for cryogenic condensations. The partial pressures were monitored by IR spectroscopy. The chopper described previously[7,8] is 47.1% open and 52.9% closed. The CW laser was set on the P-18 (946 cm^{-1}) line which is resonant with the ν_3 fundamental of BCl_3 at 953 cm^{-1}.

Figure 1 compares results for chopped and unchopped irradiation of mixtures of 100 torr of BCl_3 and 50 torr of $COCl_2$ at 10 W and a beam diameter of 7 mm. The moles of $COCl_2$ disappearing as a function of time are compared for the chopped (50 Hz) and unchopped identical samples. The open time is plotted on the abscissa (0.471 times laser on time for chopped system). This time is directly proportional to the number of photons reaching the sample so that the effect of irradiating the system with the same number of photons for both experiments can be compared. It is noted that chopping reduces the decomposition markedly (about a factor of 5). Hence, the same number of photons irradiating the system continuously vs. that in 20-ms pulses at the same power and intensity gives different results. This is inconsistent with multiple-photon vibrational excitation of the

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