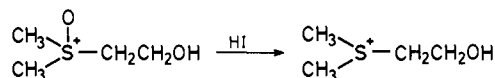


by an EI (70 eV-100  $\mu$ A, 200 °C) collision induced decomposition<sup>12</sup> (CID, He,  $p \sim 10^{-4}$  mmHg) experiment producing a CID mass spectrum identical with a computer-stored spectrum of the authentic compound. The observed behavior of the allergen in FD MS closely parallels that of the model compound trimethylsulfoxonium iodide giving rise to  $m/e$  142 ( $\text{CH}_3\text{I}^+$ ), 93 ( $(\text{CCH}_3)_3\text{S}^+\text{O}$ ), and 78 ( $\text{Me}_2\text{SO}^+$ ) 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.<sup>11</sup>



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  $\text{H}_2\text{SO}_4$ ) solution containing the triiodo ion.<sup>13</sup> 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.<sup>14</sup>

Sulfoxonium ions have never been encountered in nature before and are, except for a very few examples,<sup>15</sup> 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 $\text{CO}_2$ Laser-Induced Decomposition of Phosgene in $\text{BCl}_3$ : A Thermal Reaction

Sir:

The value of lasers for purifying materials has been demonstrated in several laboratories.<sup>1-4</sup> Of particular interest is the work of Merritt and Robertson<sup>3</sup> and later Bachmann et al.,<sup>4</sup> who showed that low-power continuous-wave (CW)  $\text{CO}_2$  laser irradiations could be utilized to selectively dissociate phosgene ( $\text{COCl}_2$ ) impurity usually present in  $\text{BCl}_3$ . While the utility of the phosgene

results cannot be disputed, the interpretations presented are open to question.

Merritt and Robertson irradiated  $\text{BCl}_3$ - $\text{COCl}_2$  mixtures having total pressures varying between 12 and 110 torr with a multiline CW  $\text{CO}_2$  laser at 100 W.  $\text{BCl}_3$  is the predominant absorber under these conditions. They found  $\text{COCl}_2$  to be decomposed quickly and selectively. On the other hand, simple heating of corresponding samples to 200 °C for several hours resulted in no  $\text{COCl}_2$  decomposition. Substituting  $\text{C}_2\text{H}_4$  for  $\text{BCl}_3$  also resulted in  $\text{COCl}_2$  decomposition, but at a reduced rate. Bachmann et al. irradiated their samples with a CW  $\text{CO}_2$  laser operating on a single P-24 ( $944.10 \text{ cm}^{-1}$ ) line at 6 W. Pressures of their static or flowing  $\text{COCl}_2$ - $\text{BCl}_3$  mixtures were always greater than 100 torr. Again,  $\text{COCl}_2$  was selectively dissociated. Replacement of  $\text{BCl}_3$  with  $\text{SF}_6$ , which is a stronger absorber than  $\text{BCl}_3$ , and irradiation with the P-20 ( $940.52 \text{ cm}^{-1}$ ) line resulted in significantly less dissociation of  $\text{COCl}_2$ . Both groups interpreted their results in terms of a nonthermal mechanism, namely, energy transfer from vibrationally excited  $\text{BCl}_3$  to  $\text{COCl}_2$ . Bachmann et al.<sup>4</sup> also expressed the possibility that a "fragmentation product of  $\text{BCl}_3$ " could be responsible for the degradation of  $\text{COCl}_2$ , with the fragment originating from direct-laser vibrational-excitational dissociation of the  $\text{BCl}_3$  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  $\text{BCl}_3$  or fragments of  $\text{BCl}_3$  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.<sup>5,6</sup>

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  $\text{BCl}_3$ . To make this distinction, we carried out on  $\text{BCl}_3$ - $\text{COCl}_2$  mixtures experiments similar to those recently made on neat  $\text{B}_2\text{H}_6$ <sup>7</sup> and  $\text{B}_2\text{H}_6$ - $\text{SF}_6$  mixtures<sup>8</sup> involving chopped and unchopped CW  $\text{CO}_2$  laser irradiations.

The samples were prepared from  $\text{BCl}_3$  and  $\text{COCl}_2$  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<sup>2</sup> 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<sup>7,8</sup> is 47.1% open and 52.9% closed. The CW laser was set on the P-18 ( $946 \text{ cm}^{-1}$ ) line which is resonant with the  $\nu_3$  fundamental of  $\text{BCl}_3$  at  $953 \text{ cm}^{-1}$ .

Figure 1 compares results for chopped and unchopped irradiation of mixtures of 100 torr of  $\text{BCl}_3$  and 50 torr of  $\text{COCl}_2$  at 10 W and a beam diameter of 7 mm. The moles of  $\text{COCl}_2$  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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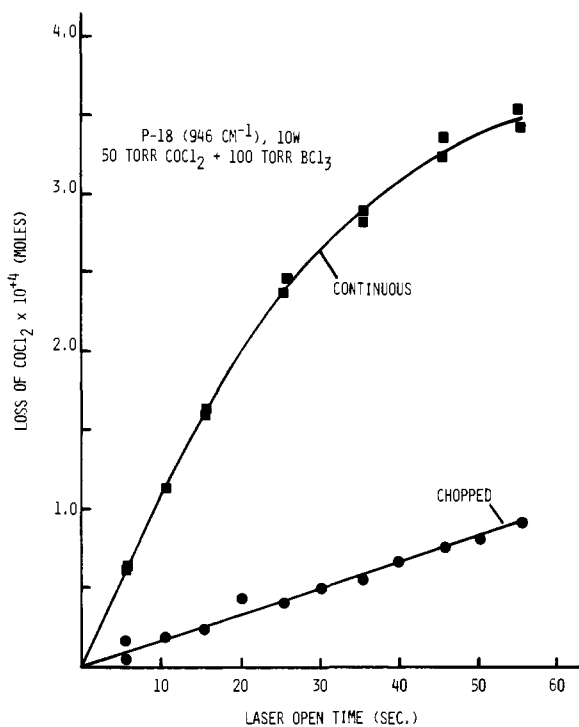
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**Figure 1.** Phosgene decomposition vs. laser irradiation time for initial partial pressures of 100-torr  $\text{BCl}_3$  and 50-torr phosgene. Power was 10 W and intensity  $26 \text{ W/cm}^2$  with the P-18 ( $946 \text{ cm}^{-1}$ ) line. The upper curve is for a continuous beam, and the lower curve is for a chopped beam.

$\text{BCl}_3$  and subsequent vibrationally controlled chemical processes. The results may be interpreted in terms of a thermally derived process in which the reaction rate is dependent upon the temperature within the beam envelope. The temperature would be lower for the chopped conditions. In this particular system,  $\text{BCl}_3$  probably exhibits additional specific catalytic activity because laser-phase homogeneous thermolysis of  $\text{SF}_6\text{-COCl}_2$  mixtures has little or no effect on  $\text{COCl}_2$  although high temperatures are produced.<sup>4-6</sup> These high temperatures would be accompanied by a corresponding vibrational distribution of molecular states. The thermal interpretation is also consistent with the findings of Meyer et al.,<sup>9</sup> who showed that  $\text{COCl}_2$  was selectively decomposed in  $\text{BCl}_3$  by an electrical discharge or radiofrequency excitation.

Bachmann et al.<sup>4</sup> attached special significance, in terms of a nonthermal mechanism, to the visible luminescence of  $\text{BCl}_3$ . We found this visually detected luminescence disappeared when the 10-W, 7-mm beam was chopped at 50 Hz. The luminescence reappeared when the chopper was slowed to about 10–13 Hz ( $\sim 75\text{--}100\text{-ms}$  pulses). Interestingly, this pulse length corresponds to that found recently for a continuous polymer pulsing in  $\text{S-F}_6\text{-B}_2\text{H}_6$  mixtures.<sup>8</sup> Interpreting this luminescence as having a thermal origin under these conditions is consistent with the delayed luminescence found by Ambartzumian et al.<sup>10</sup> and Karlov et al.<sup>11</sup> in  $\text{BCl}_3$  and the experiments of Houston et al.,<sup>12</sup> who attributed the major segment of a  $50\text{-}\mu\text{s}$  infrared double-resonance absorption signal in  $\text{BCl}_3$  to vibrational-translation relaxation.

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## Electric-Field Orientation of Poly( $\alpha$ -L-glutamic acid) in Various Conformations as Studied by Reversing-Pulse Electric Birefringence

Sir:

We wish to report the usefulness of the reversing-pulse electric birefringence (RPEB) technique, introduced by O'Konski and co-workers<sup>1-3</sup> and formulated by Tinoco and Yamaoka,<sup>4</sup> to the understanding of the electric-field orientation of poly( $\alpha$ -L-glutamic acid),  $(\text{Glu})_n$  to which the contribution of counterions is expected.<sup>5</sup> In dimethylformamide (DMF), the un-ionized  $(\text{Glu})_n$  helix possesses a large intrinsic permanent electric dipole moment along the symmetry axis ( $\mu_3$ ) in addition to an atomic and electronic polarizability anisotropy ( $\Delta\alpha = \alpha_{33} - \alpha_{11}$ );<sup>6</sup> hence, it can be oriented by an external electric field.<sup>6,7</sup> However, the orientation mechanism of  $(\text{Glu})_n$  would be complex in a salt-free aqueous solution in which the side-chain carboxylates are ionized and the conformation varies with pH. Besides  $\mu_3$  and  $\Delta\alpha$ ,<sup>8</sup> there will be field-induced dipole moments due to the counterion fluctuation<sup>9</sup> or the ionic atmosphere polarization.<sup>10</sup> A suggestion was made that the permanent dipole moment of  $(\text{Glu})_n$  is largely suppressed by a time-dependent polarizability at higher ionizations of the side-chain carboxylates.<sup>9</sup> Thus, a direct proof of the role of counterions on the  $(\text{Glu})_n$  surface should assist understanding of the polyelectrolyte behavior of biopolymers.

Theoretical calculations have illustrated that an RPEB signal ( $\Delta n$ ) should display an extremum ( $\Delta_m$ ) after a lapse of time ( $t_m$ ) upon the reversal of an applied pulse field if a molecule has both  $\mu_3$  and  $\Delta\alpha$ ; the depth depends on the ratio of  $\mu_3^2/kT\Delta\alpha$  (Figure 1 of ref 4). If a polyion has no  $\mu_3$ , a similar extremum still appears due to a time-dependent polarizability when the mobility of counterions on the polyion surface is slow; the depth depends on the ratio of the relaxation time of the counterion redistribution ( $\tau_3$ ) to that of the molecular rotation of the polyion ( $\tau_1$ ) (Figure 4 of ref 4). In either case, the extremum is undetectable if  $\mu_3 \ll \Delta\alpha$  or  $\tau_3 \ll \tau_1$ . It should be pointed out that the  $\Delta_m$ , which would be otherwise observed for a polyion such as  $(\text{Glu})_n$  with an appreciable  $\mu_3$ , becomes undetectable if the counterion mobility is much faster than the molecular rotation and if the fast-induced dipole moment is much larger than  $\mu_3$ .

Figure 1 shows oscillograms of the RPEB signal of  $(\text{Glu})_n$  and the applied pulse field in DMF and in aqueous solutions in the pH range where  $(\text{Glu})_n$  undergoes a helix-coil transition. A deep minimum ( $\mu_3^2/kT\Delta\alpha$  ca. 2)<sup>4</sup> appears expectedly in the DMF solution where  $(\text{Glu})_n$  is in the helix formation (a). In aqueous solutions, the minimum tends to be shallower with an increase of pH. At pH 4.17 (b), where  $(\text{Glu})_n$  is a complete helix showing the largest negative molar rotation, the depth is shallow as compared with that in DMF. This is a strong indication that counterion-induced dipole moments partially suppress the contribution of  $\mu_3$  to the field orientation. At pH 5.09 (c), where the helical content is usually assumed to be 100%, the minimum disappears completely. In the pH range 5.3–5.8 (d), where  $(\text{Glu})_n$  begins to change from helix to coil, the RPEB signal is complicated, showing a maximum after the pulse reversal. In the middle of

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