substituted for ethanol suggests peracids are not involved in the oxidation. Although at this time a complete reaction mechanism cannot be substantiated, it appears most likely that the products, 2-hexanone and 2-hexanol, result from a common intermediate. This suggests the metal ion catalyzed decomposition of a hydroperoxide intermediate. The common source of these two products may be $RC\text{-}(OOH)HCH_3$.

Acknowledgment. We acknowledge the support of this research by the National Science Foundation and the Office of Naval Research.

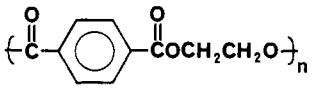
Registry No. CoSalMDPT, 15391-24-9; $RhCl(PPh_3)_3$, 14694-95-2; 1-hexene, 592-41-6; 2-hexanone, 591-78-6; 2-hexanol, 626-93-7.

Ablative Photodecomposition: Action of Far-Ultraviolet (193 nm) Laser Radiation on Poly(ethylene terephthalate) Films

R. Srinivasan* and W. J. Leigh

IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598
Received August 9, 1982

Several reports[1-6] have been published on the action of far-ultraviolet radiation (193 nm) at laser intensities on small organic molecules. All of these studies were conducted in the gas phase and showed a predominance of two-photon photochemical processes. It is possible to use the 193-nm laser source to obtain controlled one-photon transformations of a small molecule such as 2-, or 3-norcarene in dilute solutions.[7,8] In this communication, it is shown that 193-nm laser radiation leads to novel photochemical transformations in films of poly(ethylene terephthalate) (**1**, hereafter PET). Films of PET of 250 or 75 μm that were



I

free from either a plasticizer or a UV stabilizer were obtained commercially and used as obtained. The $\bar{M}_r$ was ~20 000. The excimer laser (Lambda Physik EMG500) put out pulses of 12-ns duration with intensities in the range 10-180 mJ/cm^2. A repetition rate of 1 Hz or less was used. Films of PET were exposed to the radiation in an evacuated cell through a Spurasil window. The beam was not focused on the film in order to minimize heating effects.

Single pulses of 193-nm radiation caused the etching of the surface of PET[9] and resulted in numerous gaseous products.[10] Apart from gases such as CO, CO_2, and hydrogen (which were not quantitatively analyzed) there were about 30 compounds which ranged from C_2 to C_{12}.[11] The most important of the latter set

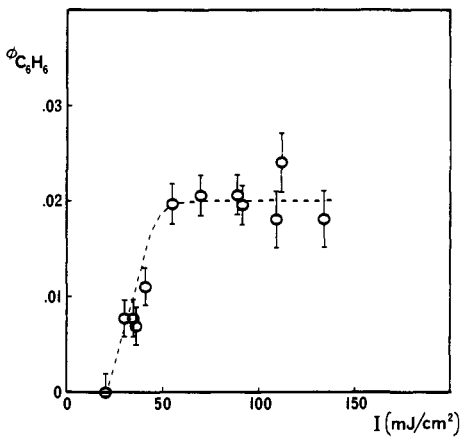


Figure 1. Quantum yield of benzene at various laser pulse intensities (wavelength 193 nm). All determinations are at constant total irradiation intensity. Gas products were *not* exposed to subsequent pulses. Since the pulse width was constant, the abscissa also represents power/cm^2.

was benzene, which was formed with a maximum quantum yield of 0.02. Toluene and benzaldehyde were also identified in yields that amounted to 1/10th of that of benzene, while ethylbenzene was formed in 1/100th of the yield of benzene. In Figure 1 the yield of benzene is plotted as a function of the intensity of the radiation. It is seen that benzene is released as a volatile product only above a threshold intensity and rapidly reaches a maximum value. The upper limit to the quantum yield of benzene may represent a balance between its formation from PET and its destruction by two-photon processes, since the mass of material that was removed by photoetching seemed to increase with intensity.

The addition of oxygen started to affect the yield of benzene only when 20 torr was present. The quantum yield of benzene was 1/7th of its value in the absence of oxygen even when 200 torr of oxygen was added. The yield of toluene showed a parallel behavior.

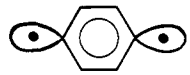
It can be calculated that if an extinction coefficient of $\sim 10^4$ L mol^{-1} cm^{-1} is assumed for the monomer unit in PET, the penetration of 193-nm radiation (for 95% absorption) would be only 2700 Å. It can also be expected that the quantum yield for bond break at this wavelength would be of the order of 0.1-1.0, as is usually the case in the far-UV photochemistry of many small organic molecules in the condensed phase at 185 nm.[8] The combination of these two factors would lead to a very high concentration of free radicals in the surface layers of the PET film shortly after a pulse of light is absorbed. The ejection of the photoproducts would result from the large free volume that the small fragments would occupy relative to the polymer chain from which they were derived. The reverse of this phenomenon is well-known from studies on the effect of pressure on polymerization reactions.[12] More recently, McBride and his co-workers[13] have elegantly demonstrated the orientational changes that follow bond break in single crystals of aromatic peresters on photolysis at low temperature. The fragments ejected from the PET film probably carry away the excess energy of the photon pulse, which would be the reason the photoetched film indicates no significant rise in its temperature. The process can therefore be termed an "ablation".[14]

The most surprising result from this study is the nature of the abstraction and recombination reactions that must occur in the PET film in order to give rise to products such as benzene, toluene,

(1) Jackson, W. M.; Halpern, J. B.; Lin, C.-S. *Chem. Phys. Lett.* **1978**, *55*, 254.
(2) Baronavski, A. P.; McDonald, J. R. *Chem. Phys. Lett.* **1978**, *56*, 369. McDonald, J. R.; Baronavski, A. P.; Donnelly, V. M. *Chem. Phys.* **1978**, *33*, 161.
(3) Sam, C. L.; Yardley, J. T. *J. Chem. Phys.* **1978**, *69*, 4621; *Chem. Phys. Lett.* **1979**, *61*, 509.
(4) Tl'ee, J. J.; Wampler, F. B.; Rice, W. W. *J. Chem. Phys.* **1980**, *72*, 2925.
(5) Turro, N. J.; Aikawa, M., Butcher, J. A.; Griffin, G. W. *J. Am. Chem. Soc.* **1979**, *102*, 5127.
(6) Duncan, M. A.; Dietz, T. G.; Smalley, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 5245.
(7) Leigh, W. J.; Srinivasan, R. *J. Am. Chem. Soc.* **1982**, *104*, 4424.
(8) Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 3412.
(9) Scanning electron microphotographs show that the etching is completely and precisely defined by the path of the light beam. There was no indication that the temperature of the film had been raised to a point where it underwent flow.
(10) Products were collected continuously during irradiation by pumping through a U-trap cooled in liquid nitrogen. Analyses were carried out on a Hewlett-Packard GC-mass spectrometer. Benzene, toluene, benzaldehyde, and ethylbenzene were identified by their mass spectra and their retention times.
(11) The intense fluorescence of one or more of the volatile components of the products when excited by 193-nm light was evident even visually in those experiments in which the products were allowed to accumulate in the cell.
(12) Weale, K. E. *Q. Rev. Chem. Soc.* **1962**, *16*, 267.
(13) Walter, D. W., McBride, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 7069, 7074 and earlier references therein.
(14) "To ablate" (verb transitive) is defined by Webster's Collegiate Dictionary (G. C. Merriam: Springfield, 1981) as "to remove by cutting, erosion, melting, evaporation, or vaporization".

0002-7863/82/1504-6784$01.25/0

benzaldehyde, and ethylbenzene. That these products are formed in the film itself is a reasonable deduction in view of the limited success that was achieved in scavenging them with oxygen.[15] Since the absorption of the light pulse followed by bond breaking is probably the fastest of the successive steps in the formation of these products, there is an interesting prospect that radicals such as **2** may be transiently present in significant concentration in the



2

PET film. This opens up interesting possibilities for the use of the far-UV laser for the synthesis of exotic radical species in frozen media.

Registry No. 1, 25038-59-9.

(15) In homogeneous gas-phase reaction, as little as 0.01 mol % of O_2 is capable of inhibiting a radical chain process. See: Benson, S. W. "The Foundations of Chemical Kinetics"; McGraw-Hill: New York, 1960; p 111. As a referee has pointed out, the present system cannot be termed homogeneous, and the pressure of oxygen at the site of photodecomposition may be far less than in the surrounding atmosphere. This would, in turn, require a modification of the statement that "the products are formed in the film itself".

A New Class of Serine Protease Inactivators Based on Isatoic Anhydride

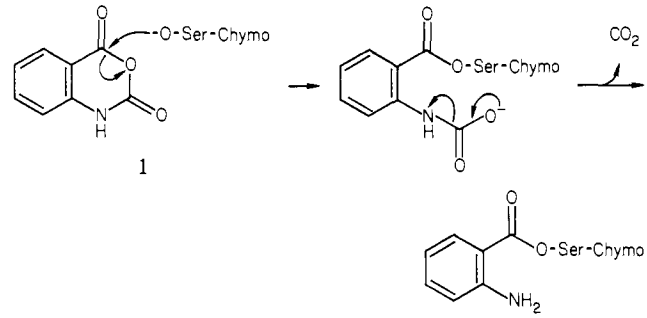
A. R. Moorman and R. H. Abeles*

Graduate Department of Biochemistry, Brandeis University Waltham, Massachusetts 02254

Received June 7, 1982

The development of suicide inactivators of serine proteases appears feasible by two general approaches. The first employs a substrate that, during the normal enzymatic process, gives rise to a reactive intermediate. This intermediate then reacts with functional groups at the active site to afford a covalent enzyme–inactivator complex. A number of compounds of this type have been reported previously.[1] The second approach utilizes a substrate that leads to a relatively stable acyl-enzyme. The studies of Caplow and Jencks[2] suggest that *p*-aminobenzoyl-α-chymotrypsin is sufficiently stable to effectively inactivate the enzyme (calculated $t_{1/2}$ for hydrolysis approximately 23 h). In agreement with this, Haugland and Stryer[3] have shown that the *p*-nitrophenyl ester of anthranilic acid gives rise to an extremely stable anthraniloyl-α-chymotrypsin. Since the same factors that cause slow deacylation of the enzyme will also decrease the rate of acylation, an efficient inactivator requires that the electron-donating properties of the amine are masked prior to acylation and become unmasked subsequent to formation of the acyl-enzyme. This suggested to us that isatoic anhydride (**1**) incorporates the essential features of this second approach. Reaction of **1** with α-chymotrypsin, as shown in Scheme I, should afford anthraniloyl-α-chymotrypsin.[4]

Scheme I. Hypothetic Scheme for Inactivation of α-Chymotrypsin by Isatoic Anhydride



1

Table I. $t_{1/2}$ (min) for Inactivation by Isatoic Anhydride

enzyme	concn of Isatoic Anhydride in preincubation mixture, μM: 12.5	125	1250
α-chymotrypsin[a]	1.2	0.5	<0.25
porcine pancreatic elastase[b]		<0.25	<0.25
α-lytic protease[c]	2.0	<0.25	<0.25
trypsin[c]	no inactivation	2.0	<1.0
papain[c]	48	2.0	<0.25

[a] α-Chymotrypsin (three times crystallized, Sigma, 50 μL of 160 μM in 1 mM HCl) was incubated in 925 μL of buffer (0.1 M potassium phosphate, pH 7.5) with 25 μL of inhibitor in 10% Me_2SO/CH_3CN. At various times, 25-μL aliquots were withdrawn, and activity was measured spectrophotometrically by adding to 925 μL of buffer and 50 μL of 11.5 mM benzoyltyrosine ethyl ester in CH_3CN. [b] Pancreatic elastase (two times crystallized, Sigma, 200 μL of 500 μM) was incubated at 25 °C in 775 μL of buffer with 25 μL of inhibitor in Me_2SO, 50-μL aliquots were withdrawn, and activity was assayed by adding to 900 μL of buffer and 50 μL of *N*-acetyl-Ala-Pro-Ala-*p*-nitroanilide (50 mM) in buffer. [c] Similar spectrophotometric assays were carried out with the remaining enzymes. The enzyme concentration was 8 μM in the incubation mixture. Buffers and substrates (with assay concentration) for the enzymes are as follows: α-Lytic protease (gift from Professor W. Bachovchin, Tufts University, School of Medicine), 0.1 M potassium phosphate, pH 7.5, *N*-acetyl-Ala-Pro-Ala-*p*-nitroanilide (2.5 mM); trypsin (three times crystallized, Worthington), 0.04 M Tris, 0.01 M $CaCl_2$, pH 8.1, *p*-toluenesulfonyl-L-arginine methyl ester (1.0 mM); papain (two times crystallized, Sigma), 0.05 M Tris, 0.005 M L-cysteine, 0.02 M Na_2EDTA, pH 7.5, α-*N*-Benzoyl-DL-arginine-*p*-nitroanilide (1.0 mM).

Preincubation of isatoic anhydride (12.5 μM) with α-chymotrypsin (8 μM) resulted in loss of 50% of the activity in approximately 1.2 min and complete inactivation in less than 6 min. At subequivalent levels of **1**, residual activity approximating the difference between enzyme and inactivator concentrations was detected (e.g., 5 μM isatoic anhydride, 8 μM α-chymotrypsin, 38% residual activity). These results suggest that the inactivation is stoichiometric. Dialysis of the inactivated enzyme against buffer (0.1 M potassium phosphate, pH 6.8, 48 h, 4 °C) resulted in the recovery of 3–5% of the enzyme activity, commensurate with the formation of a stable, covalent enzyme adduct.

The absorption spectrum of the inactivated enzyme following dialysis displayed maxima at 340 and 280 nm. With extinction coefficients of 4.0×10^3 and 5.0×10^4 cm^2/mmol, respectively,[3] a stoichiometry of one anthraniloyl moiety per α-chymotrypsin was determined. Fluorescence emission spectra of the inactivated enzyme following dialysis were found to be identical with the observations of Haugland and Stryer.[3] Taken together, these

(1) (a) Bechet, J.-J.; DuPaix, A.; Yon, J.; Wakselman, M.; Robert, J.-C.; Vilkas, M. *Eur. J. Biochem.* **1973**, *35*, 527–539. (b) Wakselman, M.; Hamon, J. F.; Vilkas, M. *Tetrahedron* **1974**, *30*, 4069–4079. (c) White, E. H.; Roswell, D. F.; Politzer, I. R.; Branchini, B. R. *J. Am. Chem. Soc.* **1975**, *97*, 2290–2291. (d) Nicolle, J. P.; Hamon, J. F.; Wakselman, M. *Bull. Soc. Chim. Fr.* **1977**, 83–88. (e) Bechet, J.-J.; DuPaix, A.; Blagoeva, I. *Biochimie* **1977**, *59*, 231–239. (f) Bechet, J.-J.; DuPaix, A.; Roucous, C.; Bonamy, A.-M. *Ibid.* **1977**, *59*, 241–246. (g) Vilkas, M. In "Enzyme-Activated Irreversible Inhibitors"; Seiler, N., Jung, M. J., Koch-Weser, J., Eds.; Elsevier/North Holland, Amsterdam; New York, 1978, pp 323–335. (h) Chakravarty, P. K.; Krafft, G. A.; Katzenellenbogen, S. A. *J. Biol. Chem.* **1982**, *257*, 610–612.

(2) Caplow, M.; Jencks, W. P. *Biochemistry* **1962**, *1*, 883–893.

(3) Haugland, R. P.; Stryer, L. *Conform. Biopolym., Pap. Int. Symp.* **1967**, *1*, 321–335.

(4) A similar strategy has been considered: Kaiser, E. T. "Bayer Symposium V"; Fritz, H., Tschesche, H., Green, L. J., Truscheit, E., Eds.; Springer Verlag: New York, 1974; pp 523–530. The *N*-*tert*-butyl-β-lactam of anthranilic acid was found to inactivate α-chymotrypsin, affording an anthraniloyl-chymotrypsin. Related compounds were found to be extremely unstable and, therefore, of limited biological utility.

0002-7863/82/1504-6785$01.25/0