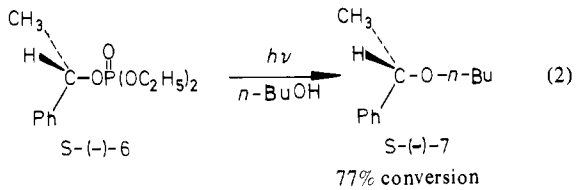


(2)

S-(-)-6 S-(-)-7

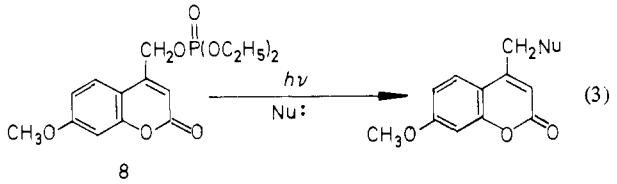
77% conversion

before:	$[\alpha]^{25}_D$ −39.7	
after:	$[\alpha]^{25}_D$ −28.5	$[\alpha]^{25}$ −4.5
	28% net racemization	5.5% net retention

is formed with a slight preference for net retention of configuration. It appears that the weakly basic phosphate anion "delivers" the nucleophile to the front face of the carbocation by a general-base catalyzed deprotonation of the solvent.[9]

Although the sequence of events proceeding to ion-pair formation is not well-defined, an argument in favor of an early development of charge separation, perhaps as early as the initial bond-breaking step, would appear reasonable. For example, examination of the relative rates and efficiencies for nucleophilic photosubstitution of a series of substituted benzylic esters indicates electron demand at the reaction center, in accord with photoionization to an electron-deficient intermediate, presumably the carbocation, both at the bond-breaking stage (based on meta- and para-substituent effects on ϕ_{dis} and k_r) and at the product forming stage (based on ϕ_{app} or k_r vs. σ).[10]

An especially intriguing application of this photochemistry was demonstrated with the coumaryl diethyl phosphate **8** which upon irradiation with 360-nm light reacted with a wide variety of nucleophilic functionalities. As illustrated in eq 3, several organic



(3)

8

Nu:
= CH_3OH (9), piperidine, cysteine, tyrosine, α-chymotrypsin, HMT

substrates were covalently "tagged" with the highly fluorescent coumaryl moiety. In addition to small molecule labeling, **8** has also been employed as a fluorescent tag fot the enzymes α-chymotrypsin and histamine *N*-methyltransferase (HMT).[13] Applications of this method for analytical, affinity labeling, and spectroscopic studies are currently being pursued.

Acknowledgment. The support of the Center for Bioanalytical Research administered by the University of Kansas and an NIH Biomedical Research Grant are gratefully acknowledged.

(9) (a) See Shiner (Shiner, V. J., Jr. "Deuterium Isotope Effects in Solvolytic Substitution at Saturated Carbon"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand Reinhold: New York, 1970; p 95) and Ritchie (Ritchie, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 3275) for discussions of general-base-catalyzed reactions of nucleophiles with carbocations. (b) Alternatively, the retention of configuration in the substitution product could have resulted by a small fraction of concerted syn attack in competition with carbocation formation, see: Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *J. Am. Chem. Soc.* **1983**, *105*, 7337.

(10) Substituent effects on the photosolvolysis of benzyl diethyl phosphates have been measured by quantum efficiency determinations and by the fluorescence efficiencies and lifetimes (Givens, R. S.; Stoner, M. R. unpublished results). The appearance efficiencies in *tert*-butyl alcohol decreased as the substituent was changed from *p*-MeO to *p*-CF_3; i.e., the efficiencies for *p*-MeO, *p*-Me, *m*-Me, H, *m*-MeO, *m*-CF_3, and *p*-CF_3 are 0.23, 0.17, 0.13, 0.16, 0.18, 0.012, and 0.063, respectively. These efficiencies were converted into relative rate constants by use of the experimental singlet lifetimes obtained[4] by the Berlman method.[11]

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(12) Light output was measured according to the method of Hatchard and Parker (Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518).

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Timed Release of Chemicals from Polypyrrole Films

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Research on the controlled release of drugs has made it possible to slowly release many chemicals at a constant rate and to spacially target the release. We have thought it would be worthwhile to learn how to control the release so that it could be turned on and off or adjusted as desired, and in several recent papers we have described neurotransmitter release from a polymer-coated electrode.[1] The neurotransmitter was covalently bound to the polymer backbone so it remained on the polymeric electrode surface until it was released by a pulse of cathodic current.

It was hypothesized that larger quantities of material could be promptly released using a conductive polymer than from the nonconducting polymers previously employed, and described here is the first example of application of conductive polymers to this problem.[2] Many of these polymers can be switched from a conductive ("doped") form containing ions to a neutral insulator state. If during the transformation from the charged to the neutral form the dopant ions were promptly flushed out, then a method for releasing ions could be developed.

The conductive polymer chosen was polypyrrole (PP). A number of electrochemical studies of PP have demonstrated that it can be readily deposited by electrochemical oxidation of pyrrole[3-5] and that the polymer can be cycled electrochemically between the charged and neutral states. Recently the utility of PP as a chloride ion gate membrane was described indicating the potential for success in our endeavor.[6] As dopants we chose ferrocyanide (FCN) or glutamate (Glu). Glu release is of interest to neuroscience and the FCN electroactivity provided a convenient way of studying the conductive films and detecting the excluded material after the reduction of the PP films.

For glutamate delivery, PP holding Glu counterions was needed. Since pyrrole did not polymerize when oxidized by using sodium glutamate as an electrolyte, PP was anodically deposited on a glassy carbon electrode from an aqueous solution containing sodium perchlorate. This coated electrode, which had the voltammetric properties expected from the literature, was then transferred to an aqueous solution containing only sodium glutamate (0.1 M, pH 6.95). A potential/time square wave was applied between the limits of 0.0 and −1.0 (SCE). at −1.0 V the film was reduced; at 0.0 V it was reoxidized. In principle this would force out ClO_4^- and replace it with Glu, and, indeed, the cyclic voltammogram of GC/PP electrodes was changed by this procedure. The fact that the cyclic voltammogram of GC/PP electrode changed when the film was "loaded" with Glu, and was restored to its original shape in a perchlorate solution, encouraged us to carry out a

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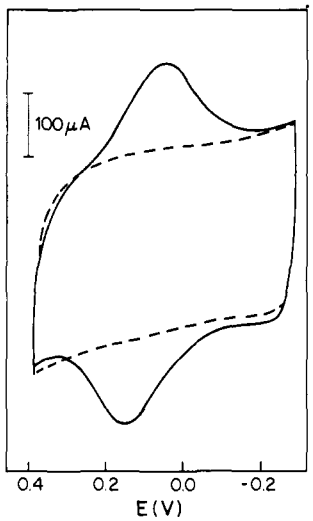

Figure 1. Cyclic voltammetry of 1 μm PP/FCN before (solid curve) and after (dashed curve) a cathodic pulse to −1.0 V for 2 min; ν = 100 mV s^{-1}.

preparative-scale release experiment.

A glassy-carbon rod coated with ~5 μm of PP, rinsed with water, and loaded with Glu, in the manner described above, was then washed for 2 min in aqueous 0.1 M NaCl solution. The electrode was transferred to another aqueous NaCl solution where a 2-min cathodic pulse (−1.0 V) released Glu. This electrode was than reloaded and washed, and Glu was again released into the same solution. Amino acid analysis showed that 2.7×10^{-8} mol cm^{-2} of electrode area had been released. That is about 200 times greater than the amount of Glu released per cm^2 from the device previously reported.[1] In a control experiment the PP/Glu electrode was prepared and used identically, except that no current was passed. Only 1.9×10^{-9} mol cm^{-2} of Glu was released.

For ferrocyanide (FCN) release, polypyrrole films were deposited from aqueous 0.05 M sodium chloride solutions that were 0.05 M in pyrrole and 0.01–0.03 M in FCN by anodic oxidation at 0.7 V onto glassy carbon electrodes.[7] The coated electrode was transferred to an aqueous solution containing only the NaCl electrolyte and a typical cyclic voltammogram ($\delta \sim 1$ μm) is shown in Figure 1. Well-defined waves for the FCN redox couple are superimposed on the large PP background. Integration of the peak current gave an estimated value for the amount of electroactive FCN in the polymer as 3.2×10^{-8} mol cm^{-2}. The FCN redox waves were stable to cycling within potential range of −0.3 to +0.4 V. After soaking the coated electrode for 17 h in buffered pH 7 solution, the peak current decreased only to 94% of its initial height.

Of interest is the voltammetric behavior of PP/FCN as a function of the thickness (δ) of the films.[8] When $0.1 < \delta < 1$ μm, both the peak current and the apparent coverage increased linearly with the increasing of the film thickness ($r > 0.999$), and the oxidation and reduction peak potentials were constant. When the thickness of the film exceeded ca. 1 μm, $E°$ was nearly constant, but E_p increased, and the peak currents were smaller than the value predicted by the linear correlation. Stepping the potential for ca. 2 min to −1.0 V caused a dramatic change in the voltammetric response of the film. The redox couple of FCN at ~0.1 V disappeared (Figure 1) indicating the exclusion of FCN anions during the reduction of the film.

The crucial experiments involved measuring the amount of FCN released and demonstrating that the amounts released could be completely controlled. A four-electrode small-volume cell was constructed[1c] in which a 50-mL droplet of electrolyte was held between a carbon (GC) disk electrode and an upright ring (Pt)–disk (GC) electrode. The disk had been previously coated with PP/FCN film. A constant-potential pulse (−0.8 V vs. Ag/AgCl) was applied to the disk for 2 min. The ring was then made the working electrode, and by cycling the potential of the ring from −0.1 to +0.6 V, FCN was detected as desired. In a control experiment the cell was assembled as usual, but no current was passed. No FCN was found in solution. Hence the release of FCN is triggered by the reduction of the film. No evidence for a spotaneous ion exchange between FCN in the film and other anions in the solution was found.

Table I. Yield of FCN Released from GC/PP/FCN[a]

δ,[b] μm	C, nmol cm^{-2} [c]	C,[d] mM
0.11	2.58	0.024
0.53	10.2	0.094
0.52	10.5	0.096
1.05	20.3	0.173[e]
0.98	19.8	0.182
3.31	38.1	0.35
3.36	46.5	0.43

[a] The disk was pulsed for 2 min at −0.8 V (vs. Ag/AgCl 3 M KCl). The volume of the droplet was 50 μL. [b] The thickness was estimated taking 24 mC cm^{-2} equivalent to 0.1 μm. [c] Surface concentration of the FCN. [d] Solution concentration of FCN after release. [e] The volume of droplet was 70 μL.

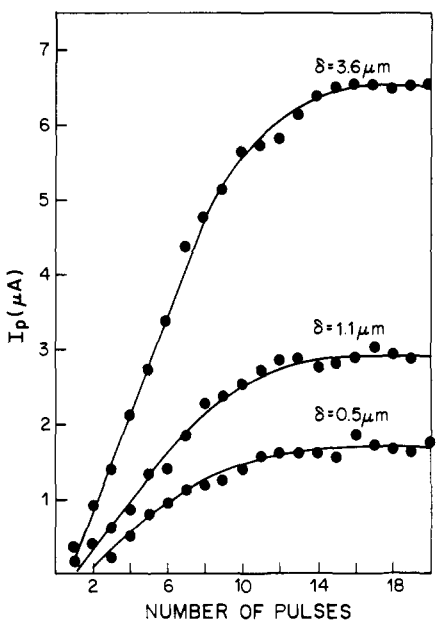

Figure 2. Variation of the peak currents of FCN released from PP as a function of number of pulses (1 s, −0.8 V vs. Ag/AgCl). The volume of droplet was 50 μL of 0.1 M NaCl unbuffered aqueous solution.

In further experiments, the amount of FCN released was quantitated in various film thickness. The results shown in Table I indicate that the amount of released material was proportional to the thickness of the film, when $\delta < 1$ μm. It was also of interest to apply short pulses to GC/PP/FCN and to check the amount of the released material to demonstrate the ultimate goal of quantitative control. By use of the small-volume cell the coated disk was pulsed for 1 s (at −0.8 V). After each pulse a CV using the ring was taken. In this way the profile of FCN concentration as a function of time was obtained. The results are shown in Figure 2. The peak current from released FCN is plotted vs. the number of pulses for different thickness of films. The amount of the released FCN increased to a constant value after about 12 pulses and the total amount of the released FCN after these 12 1-s pulses was in agreement with the amount found previously for a 2-min pulse.

These results quite clearly demonstrate that polypyrrole can be electrically controlled to release quantitatively specified amounts of anions. The total amounts released are much larger than those

(7) The conductivity of dry PP/FCN free-standing films (~50 μm) was 5–10 Ω^{-1} cm^{-1}.

(8) The "thickness" was estimated from the number of coulombs used for deposition and the value 24 mC cm^{-2} from: Waltman, R. J.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1459.

previously[1] reported, and this is the first report in which repetitive pulses have been used to consecutively release small amounts. Continuing work will explore the generality and details of release as well as develop specifically useful devices.

Acknowledgment. This work was supported by the National Institutes of Health.

Registry No. ClO_4^-, 14797-73-0; NaCl, 7647-14-5; Glu, 56-86-0; FCN, 13408-63-4; carbon, 7440-44-0; pyrrole, 109-97-7.

Dimethylsilanone Enolate

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The widespread interest in compounds containing multiply bonded silicon is clearly illustrated in the current literature.[1-6] Numerous efforts to generate and characterize these elusive species have been described, culminating in the first stable silaethylene recently reported by Brook and co-workers.[7] Parallel efforts in the theoretical community have likewise provided a fascinating picture of silicon–oxygen, silicon–carbon, and silicon–silicon multiple bonds which has occasioned a lively debate concerning the relative stabilities of the corresponding silylene tautomers.[8-11] Among the more commonly studied examples of multiply bonded silicon–oxygen compounds is dimethylsilanone, $(CH_3)_2Si{=}O$.[12] This second-row analogue of acetone is frequently invoked as an intermediate in polysiloxane and silaoxetane pyrolysis[13] and was recently identified in a low-temperature matrix as a reaction product from dimethylsilylene and N_2O.[14]

We describe here the formation and reactivity of the enolate ion of dimethylsilanone (**1**), which has been generated in the gas phase by collision-induced dissociation (CID) of trimethylsiloxide anion. Ion–molecule reactions and consecutive CID experiments are described that illustrate marked differences in the chemistry of **1** relative to its carbon analogue, $CH_3COCH_2^-$.

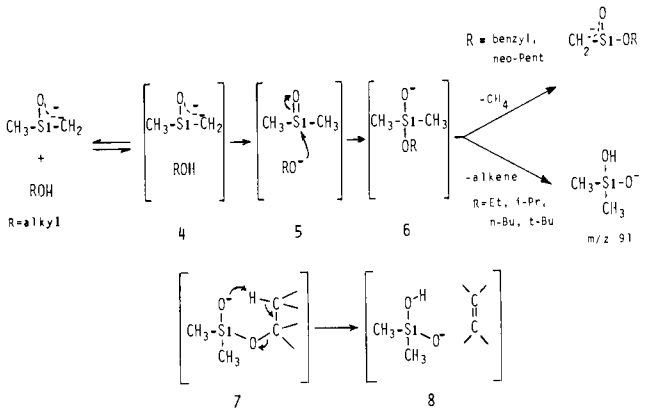
All experiments were carried out with a prototype Nicolet FTMS-1000 described previously.[15] Trimethylsiloxide anion, $(CH_3)_3SiO^-$, is initially formed by the DePuy reaction between OH^- and tetramethylsilane.[16] Following a 1.0-s interval to permit buildup of ion intensity, a 7.35-V, 0.1-ms resonant CID pulse is applied to $(CH_3)_3SiO^-$, and a 35-ms delay is allowed for its collisional dissociation against argon at ca. 5×10^{-6} torr.[17] A single daughter fragment ion is produced (m/z 73), which is shown to be due solely to methane loss by exclusive production of an m/z 75 daughter ion, **2**, when the in situ ^{18}O-labeled trimethylsiloxide ion is dissociated under identical conditions (eq 1).[18] This fragmentation pathway is analogous to methane loss from *tert*-butoxide ion which can be induced either by collisional activation[19] or photodissociation.[20] Application of a subsequent CID pulse to m/z 73 results in its further fragmentation via methyl cleavage to give CH_2SiO^- (m/z 58).

Table I. Reactions of Dimethylsilanone Enolate with Brønsted Acids

entry	ref acid	ΔH_{acid}[a]	proton transfer obsd?	other ions (m/z)[c]
a	CH_3OH	379.2	no	
b	CH_3OD		no	
c	CH_3CH_2OH	376.1	no	91
d	CH_3CH_2OD		no	92 (93)[b]
e	$(CH_3)_2CHOH$	374.1	no	91
f	$(CH_3)_2CHOD$		no	92 (93)[b]
g	$(CD_3)_2CDOD$		no	93
h	$CH_3CH_2CH_2CH_2OH$	374.0	no	91
i	$(CH_3)_3COH$	373.3	no	91
j	$(CH_3)_3CCH_2OH$	371.8	no	145
k	$C_6H_5CH_2OH$	369.6	no	165
l	$C_6H_5NH_2$	367.1	no	166
m	CF_3CH_2OH	364.4	yes	
n	CH_3SH	359.0	yes	

[a] kcal/mol; ref 24. [b] Secondary product ion derived from further reaction of m/z 92 with deuterated alcohol. [c] All reactant/product ion relationships confirmed by double resonance.

Scheme I



$$H_2O^{18} \xrightarrow{e^-} HO^{18}- \xrightarrow{(CH_3)_4Si} (CH_3)_3SiO^{18}- \xrightarrow{CID} CH_3Si(O^{18})-CH_2 + CH_4 \quad (1)$$

2

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