

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 100, NUMBER 21

OCTOBER 11, 1978

Monolayer Films of Surfactant Ester Derivatives of Tris(2,2'-bipyridine)ruthenium(II)²⁺

G. L. Gaines, Jr.,* P. E. Behnken, and S. J. Valenty*

Contribution from the General Electric Company Corporate Research
and Development, Schenectady, New York 12301. Received March 20, 1978

Abstract: Surfactant ruthenium complexes are attracting attention as potential photoinduced electron-transfer reagents, especially for possible light energy storage schemes. The ester derivatives $\{(\text{bpy})_2\text{Ru}^{\text{II}}[\text{bpy}(\text{COOR}_1)(\text{COOR}_2)]\}^{2+}$ (where bpy = 2,2'-bipyridine, the carboxy substituents are in the 4,4' positions, and $\text{R}_1 = \text{R}_2 = \text{C}_{18}\text{H}_{37}$ (I); $\text{R}_1 = \text{C}_{18}\text{H}_{37}$, $\text{R}_2 = \text{H}$ (III); and $\text{R}_1 = \text{C}_{18}\text{H}_{37}$, $\text{R}_2 = \text{C}_2\text{H}_5$ (IV)) have been prepared and characterized. The alkaline hydrolysis of I to octadecanol and III ($\text{R}_1 = \text{R}_2 = \text{H}$), with III as an intermediate product, proceeds more rapidly in monolayers and in 50% aqueous THF than does that of the water-soluble analogue V ($\text{R}_1 = \text{R}_2 = \text{C}_2\text{H}_5$) in aqueous solution. Both the surface pressure-area characteristics and luminescence of monolayers of the surfactant compounds spread on aqueous subphases depends strongly on dissolved anions; even traces of strongly interacting anions such as perchlorate lead to condensation of the films, while luminescence is ~ 20 -fold more intense in the presence of perchlorate as compared with chloride. When the monolayers are transferred to glass slides, the pretreatment of the glass affects the extent of dark ester hydrolysis. Prolonged photolysis of monolayer assemblies on glass in contact with water leads to a slow (quantum yield, $\sim 5 \times 10^{-6}$) nonhydrolytic degradation of the complex, but to no detectable water dissociation (quantum yield for H_2 production, $\leq 1 \times 10^{-4}$).

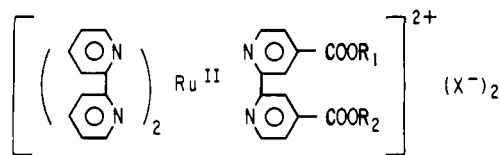
Introduction

The photophysics and photochemistry of the tris(2,2'-bipyridine)ruthenium(II) cation, $\text{Ru}(\text{bpy})_3^{2+}$ and its derivatives are currently subjects of intense interest.¹ The excited state of this complex can serve as either an electron donor² or an electron acceptor,³ and it has been demonstrated that photoinduced electron transfer from it to an electrode can occur.⁴ The visible luminescence of $\text{Ru}(\text{bpy})_3^{2+}$ in fluid solutions at room temperature has provided a useful tool in elucidating these processes. Since the complex absorbs light over a substantial portion of the visible spectrum, and its excited state is relatively long-lived and possesses enough energy in principle to produce H_2 from water, it has attracted attention as a model for practical solar energy conversion and storage schemes. It has, for example, been shown that $\text{Ru}(\text{bpy})_3^{2+}$ can be used to convert light to electrical energy in a photogalvanic cell involving the photoinduced reduction of Fe^{3+} .⁵

While high energy products of photoinduced electron-transfer reactions can in some cases be produced with good efficiency, it is generally found that rapid back-reaction occurs, degrading the stored energy. If the electron transfer occurred across a phase boundary, such a dissipative back-reaction might be impeded. It is well known, of course, that the only light energy storing process which operates efficiently in nature, photosynthesis, has its initial stages localized in membrane structures which constitute intracellular lipid-aqueous interfaces. For these reasons, the study of surfactant, and therefore interfacially localized, derivatives of such photoinduced electron-transfer reagents as $\text{Ru}(\text{bpy})_3^{2+}$ is attractive.

Surfactant ester derivatives of $\text{Ru}(\text{bpy})_3^{2+}$ were first synthesized by Sprintschnik et al.,⁶ who also reported that monolayer assemblies containing these compounds catalyzed photodissociation of water; this observation, however, has not been successfully reproduced.^{7,8}

In this paper, we present an account of our observations on the preparation, monolayer properties, and some chemical and photochemical reactions of several ester derivatives of the type shown (I-V).



Ia	$\text{R}_1 = \text{R}_2 = \text{C}_{18}\text{H}_{37}$, $\text{X} = \text{ClO}_4$
Ib	$\text{R}_1 = \text{R}_2 = \text{C}_{18}\text{H}_{37}$, $\text{X} = \text{Cl}$
II	$\text{R}_1 = \text{R}_2 = \text{H}$, $\text{X} = \text{Cl}$
III	$\text{R}_1 = \text{C}_{18}\text{H}_{37}$, $\text{R}_2 = \text{H}$, $\text{X} = \text{Cl}$
IV	$\text{R}_1 = \text{C}_{18}\text{H}_{37}$, $\text{R}_2 = \text{C}_2\text{H}_5$, $\text{X} = \text{ClO}_4$
V	$\text{R}_1 = \text{R}_2 = \text{C}_2\text{H}_5$, $\text{X} = \text{ClO}_4$

Experimental Section

Synthesis and Characterization. Full details of the preparation of compounds I-V, which followed literature procedures⁸ with minor variations, as well as characterization data, are given in the supplementary material.

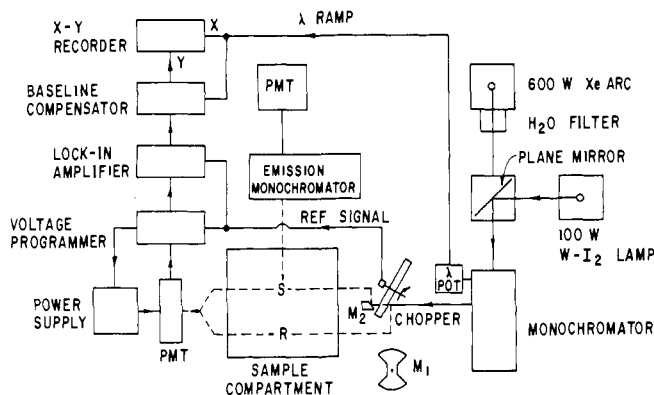


Figure 1. Block diagram of spectrometer in absorption mode operation. Flexible fiber optic connections shown as dotted lines. M_1 and M_2 are the rotating and stationary mirrors, respectively. S and R refer to the position of the sample and reference cells, respectively. For fluorescence mode operation, the plane mirror is removed and the Xe arc light source is used. Lenses, masks, diffusing screens and filter holders are not shown.

Monolayer Techniques. Monolayers were spread on aqueous subphases (in general fresh for each experiment) from dilute ($\sim 10^{-3}$ M) chloroform solutions; reproducible results were obtained by applying small drops close to the surface. With some subphase solutions, notably NaClO_4 , it was found that attempts to spread to high surface density led to the formation of partially collapsed films, which exhibited anomalous and irreproducible compression curves. In all measurements reported, the initial surface density of the spread films was $< 5 \times 10^{13}$ molecules/cm². Surface pressure-area (π -A) measurements were carried out in our recording Langmuir-type film balance, and surface potentials were determined with an ionizing electrode (^{241}Am).¹³ Luminescence from spread monolayers was measured in the fluorimeter constructed by Tweet,¹⁴ equipped with a Corning No. 2434 sharp-cut filter and an RCA C31034 photomultiplier. The GaAs photocathode (type 128) of this tube has essentially constant sensitivity in the wavelength range of interest (600–800 nm), so that spectral data obtained with a set of Bausch and Lomb interference filters (peak spacing, ~ 10 nm full width at half-maximum; peak transmission, 30–49%) were normalized by merely dividing the photomultiplier signal (after subtracting the corresponding background signal) observed with each filter in place by the integrated transmission measured for that filter.

Transfer of Monolayers to Glass Microscope Slides. Stable monolayers of I–IV were transferred from a variety of subphase compositions ($20 \pm 1^\circ\text{C}$) to the bottom half of a hydrophilic glass slide (VWR No. 48300-025, $2.54 \times 5.1 \times 0.1$ cm) which had been immersed prior to film formation. Alternatively, Ia was transferred to a hydrophobic glass slide (prepared with Me_2SiCl_2) freshly coated with five cadmium arachidate layers; both the arachidate and Ia being transferred from a subphase containing 2.5×10^{-4} M CdCl_2 and 5×10^{-5} M NaHCO_3 (pH 6.5, 20°C). Transfer occurred on slow (1.3 cm/min) withdrawal, normal to the interface at constant surface pressure (30 dyn/cm) maintained by recording¹³ or manual Langmuir-type film balances, which allowed measurement of deposition ratios. The glass slides were cleaned by ultrasonic agitation (1.5 h) in aqueous Alconox (7.5 g/L, Alconox, Inc.) at 75 – 85°C , rinsed thoroughly in distilled and triply distilled H_2O , allowed to soak overnight, given a final triply distilled H_2O rinse, and dried by a hot air blower just prior to use.

High Performance Liquid Chromatographic (HPLC) Analysis of Monolayers Recovered from Slides. Monolayers of I–IV were quantitatively desorbed from the hydrophilic glass surface by soaking the slide without agitation in acetonitrile (Burdick and Jackson, “distilled in glass”) containing 0.015 M MeSO_3H and 0.5% (v/v) HOAc for 30 min (20 – 25°C) in a Teflon block with a slot which holds ~ 2.5 mL of solution with a slide in place. The solution was transferred to a vial and additional acetonitrile ($\text{MeSO}_3\text{H}/\text{HOAc}$) solvent used to rinse the slot and the slide. The combined solutions were evaporated to near dryness with a N_2 stream at 50°C . Immediately prior to HPLC analysis, the residue was dissolved in 100 μL of 50% aqueous THF (0.015 M MeSO_3H + 0.5 (v/v) HOAc), the solution taken up in a syringe, and the vial rinsed with ~ 30 μL of fresh acidic aqueous THF and the combined solutions were injected into the chromatograph. The

conditions for the analysis of Ru surfactants have been previously described.⁹

Monolayer Spectrometer. An optical spectrometer for recording the absorption and fluorescence spectra of weakly absorbing systems, such as glass supported monolayer films of I–IV, has been constructed in this laboratory.¹⁵

Absorption Mode. The block diagram of the instrument is shown in Figure 1. The emission of the tungsten halogen lamp (Osram) is passed through a monochromator (Schoeffel GM 100) and chopped to provide alternative (31 Hz) illumination of the ends of two entrance flexible fiber optics (American Optical UV fiber). Sample holders are fixed on top of a podium which can be rotated and translated in the X, Y, Z directions. The light leaves the housing by two branches of a bifurcated flexible fiber optic and is delivered by the randomly mixed bundles of the common end onto the side window photomultiplier tube (HTV R818). The modulated dc voltage developed across a load resistor is fed into a lock-in amplifier (PAR 128) where the synchronous ac signal is detected and amplified. In order to maintain a constant detection sensitivity per unit wavelength, the PMT reference signal is fixed by regulating the gain of the PMT via a feedback loop which also includes a programmable PMT dynode voltage power supply (Gencom HM 1500), current integrator, and voltage limit. A high linearity 10-turn potentiometer coupled to the monochromator wavelength drive provides a 0–5 V dc ramp to both the baseline compensator and the X axis of the X–Y recorder (HP 2FAM) employed to register the spectrum. As the instrument is routinely used, the ordinate linearly records the absorption of a sample material with respect to a reference material, $A = 1 - I/I_0$. Normal operation begins by optically balancing the sample and reference paths with a “blank” in each at 500 nm utilizing the micrometer screw driven vernier adjustment which moves only the entrance reference fiber optic in and out along the optical axis. By varying the distance between the ends of the entrance and exit reference fiber optics, the cross-sectional area of the cone of light delivered by the former and seen by the latter is changed. Hence, a sensitive, precisely controlled, and wavelength independent attenuation has been achieved. After recording the “blank” spectrum, the blank is replaced with the absorbing sample and the final spectrum is scanned.

The accuracy of the wavelength scale has been checked by three methods: (1) low pressure Hg lamp emission, (2) didymium glass (Corning 5120) and (3) holmium oxide glass (Corning 3131). Employing a standard spectral band pass of 1.7 nm, the precision at which these settings can be reproduced is ± 1 nm. The photometric scale was established by using neutral density filters calibrated at 500 nm (Special Optics, Cedar Grove, N.J.) and checked for accuracy using solutions of cobaltous ammonium sulfate.¹⁶ The smallest absorption which could be detected at a fixed wavelength corresponded to an optical density $\approx 1.0 \pm 0.5 \times 10^{-4}$ ($S/N = 2$, $TC = 30$ s). Because of the requirement of a long time constant (10 s) and irregular baseline deviations (± 0.001 OD between 400 and 780 nm) arising from optical path dissimilarity, the smallest detectable optical density is $\approx 1.0 \pm 0.3 \times 10^{-3}$ units under standard scanning conditions (24 nm/min). The photometric scale proved linear to ≈ 2.0 OD at 510 nm.

Fluorescence Mode. By removing the plane mirror in front of the light sources, the instrument is readily converted from absorption to fluorescence mode. The chopped and monochromated exciting light (Hanovia 981C-1) is directed onto the entrance sample fiber optic. The fluorescence emitted is collected at right angles to the excitation beam by a second flexible fiber optic, focussed on the entrance slit of a second grating monochromator (Schoeffel GM 100) and detected by an end-on PMT (EM1 9658R, S-20 cathode) fitted with magnetic lenses and operated at -78°C with a fixed dynode voltage. The chopped PMT signal is amplified by the lock-in amplifier (PAR 128) and the output displayed on an X–Y recorder also coupled to the wavelength drive of the monochromator.

The instrument records uncorrected emission and excitation spectra. The sensitivity is kept constant on a day-to-day basis by comparison with a standard fluorescing compound; either rhodamine B in a polished plastic medium (1 cm², Applied Photophysics Ltd., London) for solution measurements or a yellow CS 3-70 glass filter ($2 \times 1 \times 0.035$ in., Corning) for glass supported monolayer work. The accuracy of the emission monochromator’s wavelength scale was checked by replacing the Xe arc/excitation monochromator combination with a low pressure Hg arc and inserting a MgO reflector at a 45° angle in the sample position.

The light flux into the sample compartment from the Xe arc through the excitation monochromator and fiber optic was measured with a calibrated thermopile (Reeder RSL-2C). With the exception of the Xe emission at 465–470 nm, the light flux varies from 3 to 8×10^{-12} einsteins/s (half band width, 4.2 nm) over the 400–800-nm wavelength region. Emission and excitation spectra have been manually corrected in the standard manner.¹⁷

Photolysis of Glass Supported Monolayers. The optical train in the photolysis apparatus is composed of (1) Hg/Xe arc (Hanovia 977B1, under-run at ~ 700 W, parallel beam output), (2) 10-cm circulating H₂O filter, (3) filter holder, (4) thermostated brass cell holder, (5) grating monochromator (McKee-Pedersen MP-1018, Czerny-Turner, $f/8$, 590 line/nm, 300-nm blaze, 2.8-nm band pass) and (6) thermopile (Reeder RSL-2C, $10.10 \mu\text{V}/\mu\text{W}$). The spectral distribution and incident light intensity at the photolysis cell were measured by monitoring the thermopile output as a function of wavelength and ferrioxalate actinometry,²⁰ respectively: 300–900 nm ("white light"), $I_0^i \sim 1.7 \times 10^{18}$ quanta/s, Pyrex ($l = 0.32$ cm) + soft glass ($l = 0.1$ cm). The ferrioxalate calibrated (at 366 nm) thermopile output was used to correct for day-to-day variations in the arc emission.

The four demountable sides (0.5×0.5 in.) of the photolysis cell were machined from Teflon to accept two glass slides as windows in channels allowing a separation of either 0.1 or 0.5 cm. Teflon tape was used as gasket material around the perimeter of the slides. The cell was held tightly together with four nylon screws. The interior of the cell was accessed through a double septum seal in the top. The monolayer photolyses were done with a 0.1-cm window separation where the total cell volume is 1.0 mL, while the 0.5-cm separation was used for the ferrioxalate actinometry. The assembled cell fitted snugly into the thermostated cell holder and was masked such that only the bottom half of the windows, i.e., the monolayer coated areas, were illuminated.

For each photolysis experiment three sets of two slides each were coated simultaneously from the same film spread at the air-subphase interface. In turn, each pair of slides was assembled into the photolysis cell and the monolayers on the outer sides wiped off using cotton swabs moistened with acetonitrile (0.015 M MeSO₃H + 0.5% (v/v) HOAc). The three sets were used for: (1) the photolysis in contact with an aqueous solution, (2) the dark, wet control, and (3) the dark, dry control.

For the photolysis set, an absorption spectrum of the dry cell was recorded. The cell's interior was purged with N₂ (10 min) and then filled to overflowing with deaerated aqueous solution (boiled and then cooled under N₂) via a gas tight syringe. In some instances, a second absorption spectrum was recorded before placing the cell in the holder (20 ± 1 °C) and irradiating. After the photolysis, a 25- μL aliquot of the cell's contents was obtained through the septum with a "Pressure-Lok" Series A-2 syringe (Precision Sampling), which has a valve behind the needle such that samples can be transferred in the syringe barrel without gas loss, and analyzed by VPC for dissolved H₂ according to an established procedure.¹⁰ The remaining aqueous solution was removed from the cell and analyzed for soluble Ru^{II}(bpy)₃²⁺ derivatives by HPLC⁹ and absorption spectrometry. The still assembled photolysis cell was dried in a vacuum desiccator at 20–25 °C before recording another absorption spectrum. The cell was then disassembled and the supported films were desorbed from the glass surface as described earlier and analyzed by HPLC.

The dark, "wet" control slides were handled exactly as above except that the assembled, aqueous solution filled cell was stored in the dark rather than being exposed to the photolyzing light. The dark, dry control slides merely had their absorption spectrum recorded as assembled, dry, in the photolysis cell.

Results

A. Monolayer Films Containing Only I. Our most extensive results concern spread monolayers of the dioctadecyl ester; in these studies we have utilized two independent perchlorate salt preparations (1a) as well as the chloride salt (1b). Since the perchlorate salt samples exhibit identical properties, only one of them will be discussed here. The differences in behavior between 1a and 1b can be accounted for on the basis of counterion effects as will be noted. (In what follows, effects common to 1a and 1b are referred simply to 1.) The synthetic route to I involves the esterification of 4,4'-dicarboxy-2,2'-bipyridine (VI) with *n*-octadecanol and subsequent reaction with (bpy)₂-

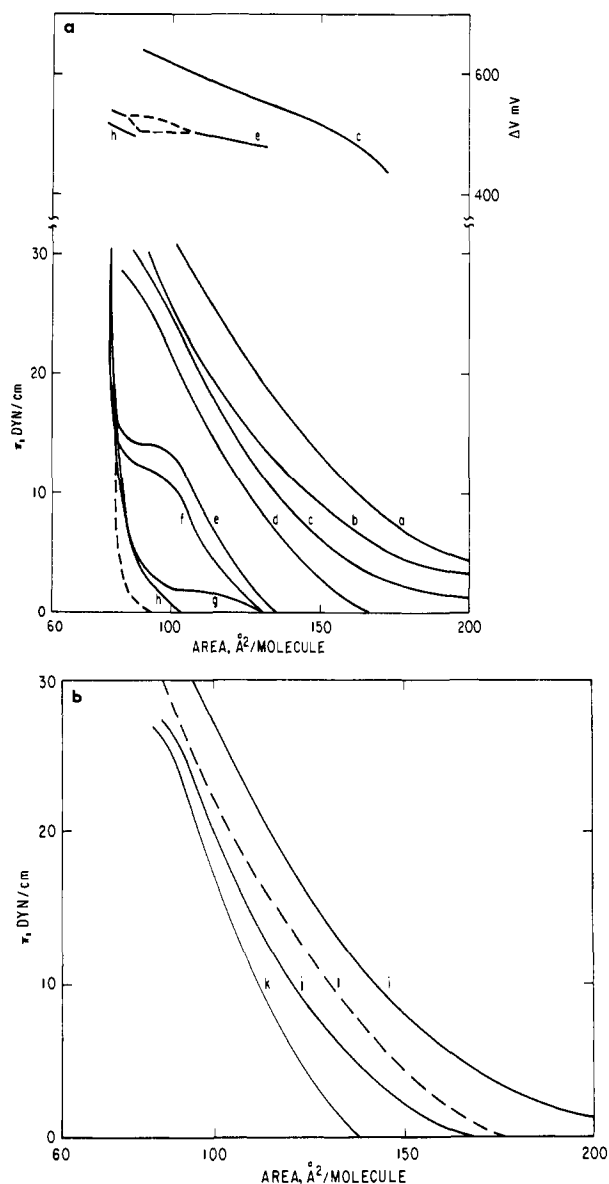


Figure 2. Surface pressure (π) and potential (ΔV) curves for Ib on aqueous subphases (0.01 M except as noted). (a) a, NaF; b, NaOAc; c, NaCl; d, NaBr; e, NaSCN (dashed lines represent limits of drifting surface potentials); f, NaI; g, NaBF₄; h, NaClO₄ (dashed curves represents expansion of film). (b) i, Na₂SO₄; j, K₄Fe(CN)₆; k, K₃Fe(CN)₆; l, 2.5×10^{-4} M CdCl₂- 10^{-5} M NaHCO₃, pH 6.8.

Ru^{II}Cl₂ (IX) in ethanol.⁸ While the synthesis employed to obtain IX resulted in poor yields (35%), elemental analyses and extinction coefficients (low by 22–79% compared with the literature),²¹ the subsequent reaction with well-characterized IV gave I as a substantially pure material (see Experimental Section) containing small amounts (<3 mol %) of {(bpy)₂-Ru^{II}[bpy(COOC₁₈H₃₇)(COOR)]²⁺ where R \equiv C₁₆H₃₃ or C₂₀H₄₁ which resulted from impurities of *n*-hexadecanol and *n*-eicosanol in the octadecanol used for esterification. Saponification and transesterification reactions, which lead to 11–V, were eliminated by avoiding contact of either I or IV with alkaline solution.

Surface Pressure and Potential. When monolayers of I are spread on alkaline subphases, the area at constant surface pressure decreases with time as the ester hydrolyzes (vide infra). However, at pH < 7, the films exhibit stable and generally reversible surface pressure-area (π -*A*) curves; both these and the measured surface potentials (ΔV) are markedly dependent on the counterions present in the subphase solution (Figure 2). On subphases giving the more expanded films (e.g.,

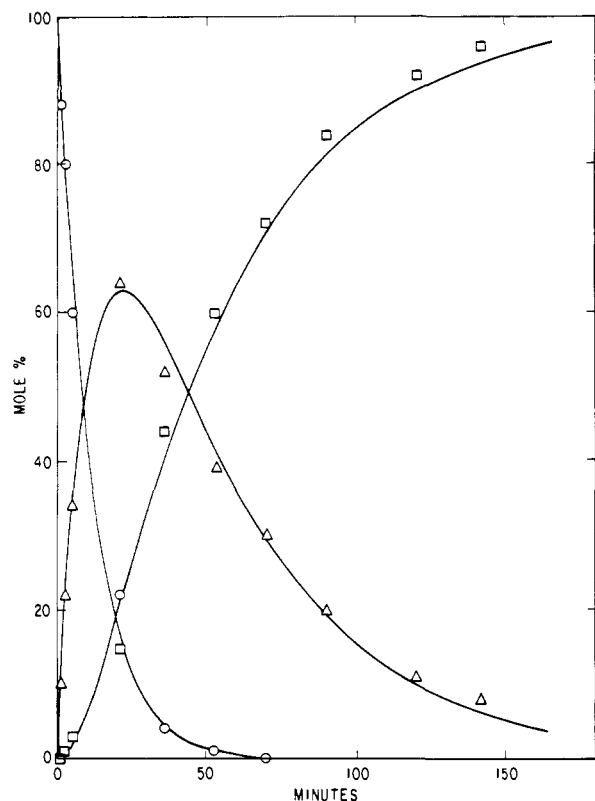


Figure 3. Relative concentrations of reactant (V), O, and products $\{(bpy)_2Ru^{II}[bpy(COOEt)(COO^-)]\}^+$; Δ , and II, \square , during hydrolysis in aqueous pH 10 borate buffer (10^{-2} M, 20 ± 1 °C, initial $[V] = 1.0 \times 10^{-4}$ M) as determined by LC. Lines—calculated for consecutive pseudo-first-order reactions, with $k_1 = 8.62 \times 10^{-2} \text{ min}^{-1}$, $k_2 = 2.16 \times 10^{-2} \text{ min}^{-1}$.

Cl^- , AcO^-), the π - A curves, and ΔV values are exactly reversible and do not vary with compression rate nor with the time the film is held at high surface pressure (at least up to 30 dyn/cm; most of our measurements have been limited to this value of π , because of the risk of leaks and subphase overflow in our apparatus at higher pressures). With the more strongly condensing counterions (e.g., ClO_4^-), some surface pressure decay is observed after rapid compression to high π , and there is a small amount of compression-expansion hysteresis in cycling (cf. the dashed curve in Figure 2a), but this hysteresis is largely reversible, since a second compression curve closely approximates the initial compression. For the ions exhibiting intermediate behavior (SCN^- , I^-), there is also some hysteresis, but the shape of the compression curve also persists on expansion and recompression cycles. (Occasionally, small humps have been noted at the beginning of the plateau region during rapid compression, they have not been observed in expansion curves, and are not reproducible on repeated cycles.) Surface potentials also exhibit drifts with time, within the limits shown in Figure 2a, over the range of areas characterized by π - A hysteresis. At both low and high surface pressures, however, the potentials are stable and reproducible.

For chloride and perchlorate anions, we have also examined the effect of counterion concentration. We can detect no difference in π - A curves for perchlorate over the range 10^{-3} -0.1 M, although ΔV decreases by ~ 50 mV for each 10-fold increase of concentration. In the case of chloride, there is a slight (1-2 dyn/cm) reduction in π at areas greater than $130 \text{ \AA}^2/\text{molecule}$ for films on 0.5 M NaCl as compared with 10^{-3} M, but, at lower areas ($\pi > 10$ dyn/cm), the curves are identical over this subphase concentration range. When films are spread on mixed chloride-perchlorate solutions, a high selectivity is observed. Thus, the curve on 10^{-2} M $Cl^- + 10^{-3}$ M ClO_4^- is

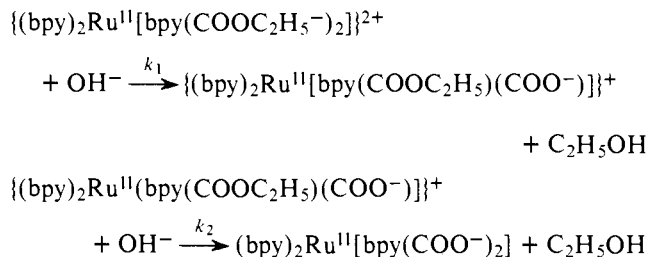
identical with that on ClO_4^- alone; for 10^{-2} M $Cl^- + 10^{-4}$ M ClO_4^- a small expansion at $\pi < 5$ dyn/cm occurs, but at higher π the curve again matches that on ClO_4^- ; on 10^{-2} M $Cl^- + 10^{-5}$ M ClO_4^- , the compression curve agrees with that obtained on Cl^- alone, but a hysteresis loop is observed on expansion in the range $30 > \pi > 17$ dyn/cm.

Even the small amount of strongly complexing anion which can be introduced by spreading Ia (which would lead to a concentration of $\sim 6 \times 10^{-8}$ M if it were uniformly dispersed in the subphase under our experimental conditions) does lead to a detectable effect; small hysteresis loops at $\pi > 20$ dyn/cm are observed when this preparation is spread on dilute (10^{-2} - 10^{-3} M) NaCl subphases, although the compression curves are identical with those of Ib.

Admixture of either arachidic acid or octadecanol in monolayers of I yields substantial deviations from additivity of molecular areas. Thus, on 0.01 M NaCl subphase, a film composed of arachidic acid + Ia, mole ratio 4.97:1, exhibits a mean molecular area at $\pi = 10$ dyn/cm of 27 \AA^2 , as compared with 41 \AA^2 required for additivity; for octadecanol + Ia, 4.93:1, the observed area is 32 \AA^2 vs. additive 40 \AA^2 .

Our results are generally similar to those recently reported by Seefeld et al.,²² although the areas observed by us are 5-10% smaller than theirs. They also observed a larger concentration effect on the π - A curves on chloride-containing subphases. Since their measurements were all made with a perchlorate salt preparation (analogous to our Ia), it is possible that this effect results from competition with the perchlorate anions introduced in spreading.

Hydrolysis of $\{(bpy)_2Ru^{II}[bpy(COOR)_2]\}^{2+}$. Our observations of film shrinkage led us to examine the alkaline hydrolysis of the esters in more detail. (No film shrinkage is observed on 0.1 M HCl.) Results for the hydrolysis of the diethyl ester (V) in aqueous pH 10 borate buffer are shown in Figure 3. The observed concentration of the monoester and dicarboxylic acid (II) are in quantitative agreement with expectation for the simple consecutive pseudo-first-order reactions



with the pseudo-unimolecular rate constants $k_1 = 8.62 \times 10^{-2} \text{ min}^{-1}$ and $k_2 = 2.16 \times 10^{-2} \text{ min}^{-1}$. In a mixture of 50% aqueous pH 10 buffer + 50% THF, the hydrolysis of the dioctadecyl ester (Ia) proceeds in a similar manner but even more rapidly, with the concentration of starting material dropping to nearly zero and the concentration of the monoester reaching a maximum within < 10 min. While the data qualitatively show the same behavior as that depicted in Figure 3, quantitative fitting requires that k_2 decrease as the second reaction proceeds; we find $k_1 \sim 1.1 \text{ min}^{-1}$, while k_2 initially $\sim 9 \times 10^{-2} \text{ min}^{-1}$, decreasing to $\sim 6 \times 10^{-2} \text{ min}^{-1}$ as the reaction nears completion.

In monolayers, the hydrolysis of Ia at the same (bulk) pH is still more rapid and the rate has been shown to increase with pH. We have followed the area change at constant surface pressure (10.4 dyn/cm, 23 ± 1 °C) and have noted that the time required for the film area to decrease to $(A_0 - A_f)/2$, where A_f is the final area (two molecules of octadecanol per molecule of starting Ia), decreases with increasing pH: pH 8.2, 29 min; 9.7, 5.6 min; 10.4, 1.9 min; and 12, < 1 min (10^{-3} M $NaHCO_3/Na_2CO_3$ solutions adjusted to the desired pH with

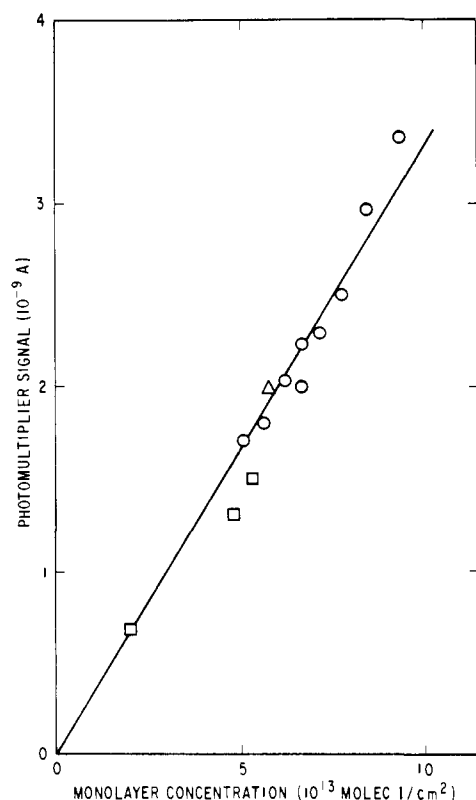


Figure 4. Total luminescence intensity of monolayers containing 1b on 0.01 M NaCl: \circ , single component films (concentration varied by compression); Δ , arachidic acid diluent; \square , octadecanol diluent. (At the lowest value, the net signal is $\sim 1.5 \times$ the background signal (no monolayer) and $S/N \sim 30$.)

HCl except pH 12 for which 0.01 M NaOH was used). We have verified that, when the reaction is complete, the residual film exhibits a π - A curve identical with that for pure octadecanol, and have shown by gas chromatography that the recovered film material is octadecanol.

Luminescence of Monolayers on Aqueous Subphases. Substantial red luminescence can be detected from spread monolayers of I in the monolayer fluorimeter. In preliminary experiments with films of the perchlorate salt spread on pure water, the intensity of the emission was not reproducible and changed with time. However, after the importance of counterions was recognized and films were examined on salt-containing subphases, luminescence was found to be reproducible and invariant with time ($\pm 10\%$ in photomultiplier current) for periods up to several hours (either in the dark or under continuous illumination with the exciting light). The total emission was found to be ~ 20 -fold greater on 0.01 M NaClO₄ as compared with 0.01 M NaCl subphase. On the NaCl subphase, where the monolayer is sufficiently compressible that significant changes in chromophore density can be achieved by film compression, it was found that luminescence is proportional to the concentration of the luminescent molecules in the monolayer (Figure 4).

The spectral distribution of the emission has been determined with interference filters (Figure 5).

Transfer of Monolayers to Glass Slides. We have been able to reproducibly transfer monolayer films of I from a variety of subphases (triply distilled H₂O, 2.5×10^{-4} M CdCl₂ + 5×10^{-5} M NaHCO₃, 10^{-3} M NaCl, 10^{-3} M NaClO₄) onto hydrophilic glass surfaces in single layers as indicated by the deposition ratio (DR), 1.0 ± 0.1 . In order to form a uniform layer on the glass (as visualized by breathing on slide), the slide must be immersed in the subphase prior to monolayer spreading and compression to allow transfer upon withdrawal

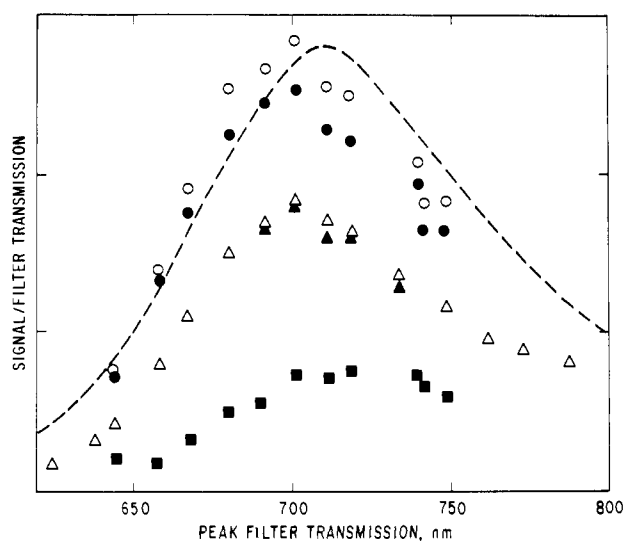


Figure 5. Spectral distribution of luminescence from 1 in monolayers. On 0.01 M NaClO₄, \circ represents perchlorate salt; \bullet chloride salt. On 0.01 M NaBF₄, Δ represents chloride salt; \blacktriangle perchlorate salt. On 0.01 M NaCl, \blacksquare represents chloride salt, signal $\times 5$. All at $\pi = 4$ -6 dyn/cm. Dashed line—luminescence spectrum of monolayer transferred to hydrophilic glass slide from 10^{-3} M NaClO₄, arbitrary intensity scale.

through the film. If the slide is dipped through the already compressed film (DR, < 0.1) and then withdrawn (DR, ~ 1) the adsorbed film contains horizontal striations (~ 1 -mm width) separated by uncovered strips. It was further noted that the line of contact of the film covered interface with the glass surface was irregular and "jumped" during immersion of the clean slide.

We were unsuccessful in attempts to build up multilayer organizes containing only pure 1a but were able to transfer 10 layers of a mixed film of 1a and cadmium arachidate (1:9 molar ratio in spreading solution) onto a hydrophobic surface. Single monolayers of 1a have been transferred (DR = 0.9 ± 0.1) to hydrophobic slides coated with five layers of cadmium arachidate (DR = 0.9 ± 0.1).

The application of HPLC to analyze the surfactants adsorbed from solid substrates has proven a powerful technique to determine the amount of material transferred to the surface and observe the chemical transformations of the adsorbed film. Transfer of monolayer films of I from either triply distilled H₂O, 2.5×10^{-4} M CdCl₂ + 5×10^{-5} M NaHCO₃ or 10^{-3} M NaCl to hydrophilic glass surfaces (14.5 ± 0.5 cm²) prepared by Alconox sonication (vide infra) should result in $2.8 \pm 0.1 \times 10^{-9}$ mol of material being adsorbed ($\pi = 30$ dyn/cm, $83 \text{ \AA}^2/\text{molecule}$). Based upon a large number of slides which were not treated in any other manner, soaking the slides in acetonitrile containing 0.015 M MeSO₃H and 0.5% (v/v) HOAc and analyzing the resulting concentrated solutions by HPLC led to a 98 ± 2 mol % recovery of 1. The sensitivity of the method allows detection of 1×10^{-12} mol of I or < 0.1 mol % of the amount of material originally transferred to the slide. The use of the methanesulfonate anion to compete with adsorbing sites on the glass surface for the dication I was suggested by the ion-pairing conditions employed in the reversed phase chromatographic separation.¹⁰ Chromatography done without such a counterion led to irreversible adsorption of the surfactant cations on the underivatized areas of the silica column packing. Acetonitrile was chosen for its ability to solubilize 1-V and MeSO₃H, its inability to participate in hydrolysis, transesterification or other chemical reactions with 1-IV, its inertness to air oxidation, and availability in high purity. Our experience with soaking the slides in pure CHCl₃ or THF (3 h, occasional agitation) shows erratic and less than quantitative recovery.

Table II. Photolyses of Glass Supported Monolayers of I^a

monolayer/subphase	exptl conditions	HPLC recovery		
		I, $\times 10^9$ mol	III, $\times 10^9$ mol	total mol % ^b
Ia/H ₂ O	<i>hν</i> , H ₂ O	1.6	0.05	59
	dark, H ₂ O	2.6	0.05	95
	dark, dry	2.8	0.01	100
Ia/10 ⁻³ M NaClO ₄	<i>hν</i> , 10 ⁻³ M NaClO ₄ + 0.1 M 2-propanol	1.9	0.06	70
	dark, 10 ⁻³ M NaClO ₄ + 0.1 M 2-propanol	3.2	0.04	115
	dark, dry	3.6	0.04	130
Ia/10 ⁻³ M NaClO ₄	<i>hν</i> , 10 ⁻³ M HClO ₄ + 0.1 M 2-propanol	3.3	0.07	121
	dark, 10 ⁻³ M HClO ₄ + 0.1 M 2-propanol	3.0	0.05	109
	dark, dry	4.0	0.04	144
Ib/10 ⁻³ M NaCl	<i>hν</i> , 10 ⁻³ M NaCl + 0.1 M 2-propanol	2.0	0.07	74
	dark, 10 ⁻³ M NaCl + 0.1 M 2-propanol	2.4	0.04	87
	dark, dry	2.8	0.04	101
Ib/10 ⁻³ M NaCl	<i>hν</i> , 10 ⁻³ M HCl + 0.1 M 2-propanol	1.5	0.07	54
	dark, 10 ⁻³ M HCl + 0.1 M 2-propanol	2.0	0.04	71
	dark, dry	2.0	0.05	71

^a Xe/Hg arc; 300 < *hν* < 900 nm; 50–150 min; Ia, $\sim 1\text{--}3 \times 10^{-4}$ einsteins; 20 ± 1 °C. ^b Total mole percent recovery $(I + III) \div 2.8 \times 10^{-9}$ mol $\times 100$; assuming $85 \text{ \AA}^2/\text{molecule}$ and DR = 1.0, the calculated amount of Ia or Ib transferred to each slide is 2.8×10^{-9} mol.

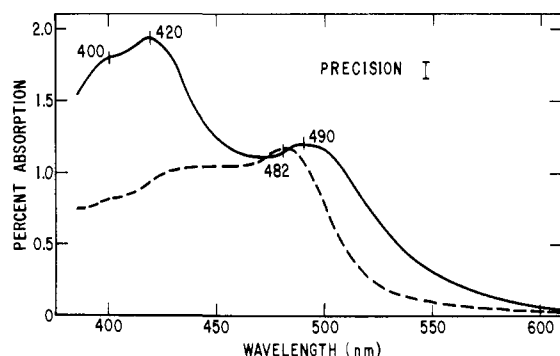


Figure 6. Absorption spectra of I as a single monolayer on both sides of a hydrophilic glass slide (—, average of 40 individual slides supporting films transferred from 10⁻³ M NaClO₄, 10⁻³ M NaCl, 2.5 $\times 10^{-4}$ M CdCl₂ + 5 $\times 10^{-5}$ M NaHCO₃, 2.5 $\times 10^{-4}$ M CdCl₂ + 1 $\times 10^{-4}$ M NaOAc, and distilled H₂O; precision, $\pm 0.12\%$; absorption, ± 3 nm) and as an equivalent number of molecules in CHCl₃ solution (- - -, 3.9×10^{-7} M, *l* = 1.0 cm).

In contrast to glass supported monolayers of Ia transferred from triply distilled H₂O or Ib transferred from 10⁻³ M NaCl which give quantitative recovery based on molecular areas and the geometrical area covered, 127–144 mol % recovery was observed for adsorbed films of Ia transferred from 10⁻³ M NaClO₄ even though the deposition ratios are 1.0 ± 0.1 in all cases.

The recovery of Ia from slides containing five base layers of cadmium arachidate has led to nonquantitative and irreproducible recovery (20–70%). If the long-chain carboxylate anion strongly ion pairs with I, the resulting salt may be insoluble in acetonitrile or, being soluble, upon injection into the LC may not elute from the reversed-phase column under the conditions used owing to the greater hydrophobic interaction of four rather than two octadecyl chains with the stationary phase.

Having established the suitability of this technique for the analysis of dry, hydrophilic glass supported monolayers of I, we observed that immersing such slides in triply distilled H₂O (pH ~ 6) led to hydrolysis (dark reaction). A variety of glass pretreatments, including flaming, solvents, and chemical washes, were tested with extremely variable results (Details are recorded in Table I in the supplementary material.) In several cases more than half of the I was converted to III after immersion for 4 h. The best glass pretreatment that we have found for minimizing hydrolysis is sonication in hot Alconox

solution; however, even with this treatment, dark hydrolysis occurs and produces III at an initial rate of ~ 2.5 mol %/h, which slows by a factor of 10 after 16-h immersion.

Optical Spectroscopy of Glass Supported Monolayers. The absorption spectra of single monolayers of Ia or Ib transferred from all subphase compositions listed previously to hydrophilic glass slides are identical within the observed experimental error. Monolayers of I transferred to hydrophobic slides coated with five layers of cadmium arachidate give spectra having $\sim 30\%$ less absorption. Figure 6 shows the spectral comparison of an equal number of molecules of Ia in CHCl₃ and as a monolayer uncorrected for reflection²³ occurring at the substrate–air interface. The excitation spectrum in CHCl₃ solution reproduces the shape of the corresponding absorption trace.

The intensity of the emission (710 ± 5 nm) from dry monolayers of I in air on hydrophilic glass was found to be dependent on the counterion in the subphase and the length of time the film remained at the air–subphase interface. Films formed on 10⁻³ M NaClO₄ give a two–threefold greater emission than those formed on the CdCl₂–NaHCO₃ subphase when both monolayers were transferred to glass at the same film age (~ 8 min). The emission of films of Ia picked up at intervals from CdCl₂–NaHCO₃ decreases to a barely measurable value when the film has aged on the aqueous subphase for 115 min, while the corresponding absorption spectra show no change. However, no further decrease over a period of hours occurs once the films are on the slides. Within our experimental error, ± 10 nm, no effects on emission maxima have been observed.

Upon immersion of these slides in distilled water, the absorption spectrum exhibits slight changes in maxima (5–10 nm) and extinction (5–25% decrease), while the luminescence is slightly blue shifted 5–10 nm and reduced 20–60%. In no case has the emission recovered more than 10% upon heating under vacuum (< 1 Torr at 35 °C for 15 h). We have observed that the emission of a film of Ia transferred from CdCl₂–NaHCO₃ subphase to a hydrophilic glass slide varies as the counterion in the surrounding aqueous solution is sequentially exchanged (environment, relative intensity at 710 nm): air, 1.0; H₂O, 0.6; 1 M NaClO₄, 1.0; H₂O, 0.7; 1 M KI, 0.0; 1 M NaClO₄, 0.7.

Our observations differ from those of Seefeld et al.²² who found that monolayers deposited on quartz slides did exhibit an increase in luminescence on vacuum drying (either with or without prior immersion in water). In view of the differences in slide preparation and other experimental details, we are unable to comment on this difference.

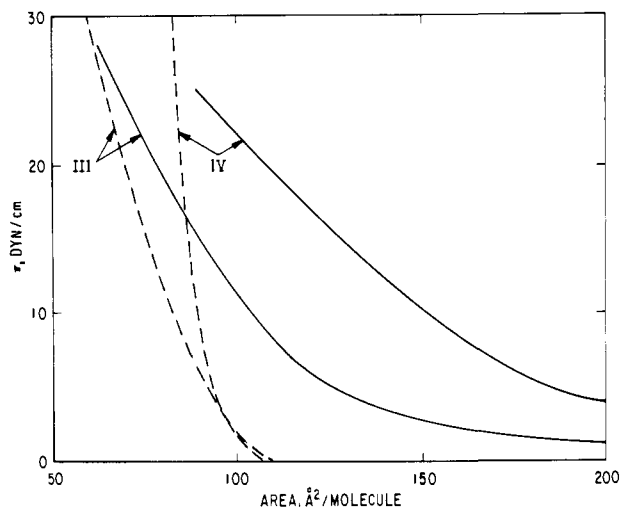


Figure 7. π - A curves for III and IV on 0.1 M HCl (—) and 10^{-3} M NaClO_4 (---) subphases.

Photolysis of Glass Supported Monolayers of I. Single monolayers of Ia and Ib on hydrophilic glass surface have been irradiated with "white" (300–900 nm) light in contact with a variety of aqueous solutions. The HPLC results of five individual experiments are given in Table II. The average disappearance quantum yield for I in these experiments is $5 \pm 2 \times 10^{-6}$. Other than small amounts (1–3 mol %) of III which are found in both the photolysis and dark, aqueous control, chromatographic analysis under currently employed conditions shows no component(s) which could account for the amount of I consumed in the photolysis. Absorption spectra of the dry monolayers taken before and after photolysis show the development of a broad band extending throughout the visible spectrum to ~ 700 nm with the original maxima still at 415 and 490 nm but superimposed on the new band and of diminished absorption. Neither HPLC analysis nor absorption spectroscopy of the aqueous photolysis solution show any trace (< 2 mol %) of II or any other water-soluble $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ derivative.

In no case was hydrogen observed by gas chromatography in these photolyses. Irradiation (254 nm) of acidic $\text{K}_4\text{Fe}(\text{CN})_6$ in aqueous 2-propanol solution¹⁰ provided a source of molecular hydrogen in known, subsaturation concentrations which established the lower limit of detectability to be $3.3 \pm 0.1 \times 10^{-9}$ mol ($S/N = 2$). Containment control experiments showed a leak rate of 2.4×10^{-10} mol of hydrogen/min when utilizing the Teflon photolysis cell. Based on this leak rate and the absorbed light flux, $\sim 3 \times 10^{-6}$ einstein/min, if any hydrogen is being produced, $\Phi_{\text{H}_2} \lesssim 1 \times 10^{-4}$.

B. Monolayer Films Containing III and IV. We have obtained samples of III and IV by treating I with alkaline EtOH or aqueous THF, respectively. HPLC analysis showed these preparations to be of high purity: 97 mol % III and 99 mol % IV. In acidic 20% aqueous THF solutions, I–IV are indistinguishable spectroscopically, possessing absorption maxima at 485 and 425 nm of the same extinction and emission maximum at 718 nm of the same intensity. In neutral 20% aqueous THF solutions, the carboxyl groups of III and IV are ionized as evidenced by an immediate, substantial enhancement and blue shift of the emission spectra (II, 647 nm, $4.0\times$ increase; III, 690 nm, $1.5\times$ increase) and a corresponding 10–20% increase in extinction and shift in the absorption spectra (II, 457, 430 nm (sh); III, 472, 435 nm (sh)). In alkaline 20% aqueous THF, Ia, IV, and also III undergo hydrolysis with the development of similar spectral shifts which finally are identical with those of ionized II. Similar spectral changes are noted for the alkaline hydrolysis of V in totally aqueous solutions.⁹

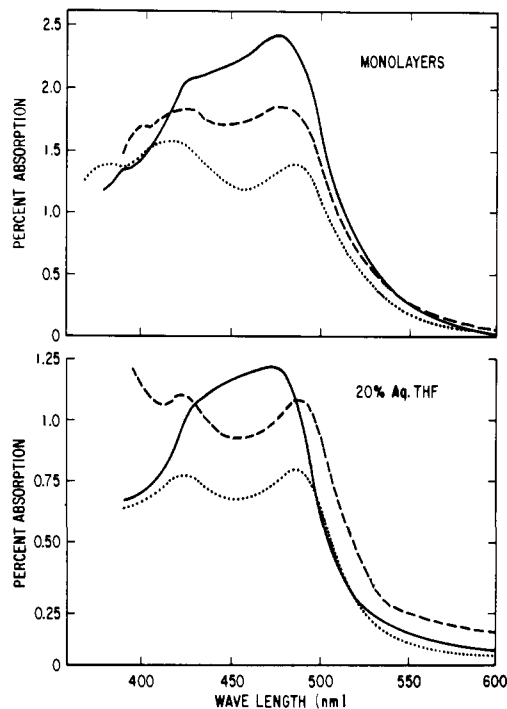


Figure 8. Upper traces: typical absorption spectra of III and IV as single monolayers on both sides of a hydrophilic glass slide transferred from 10^{-3} M NaClO_4 (---, IV on acid cleaned glass; —, III on acid cleaned glass, 99 mol % pure; and - - -, III on Alconox cleaned glass, also contains 5 mol % I and 10 mol % *n*-octadecanol). Lower traces: absorption spectra of III and IV as an approximately equivalent number of molecules in 20% aqueous THF (---, IV, 2.9×10^{-7} M, pH ~ 6 ; —, III, 5.5×10^{-7} M, pH ~ 6 ; and - - -, III, 5.5×10^{-7} M, pH ~ 2).

Surface Pressure–Area Curves. Compounds III and IV, and mixtures containing them, exhibit even more pronounced subphase sensitivity than does I. Figure 7 shows the stable and reversible π - A curves of III and IV on 0.1 M HCl and 10^{-3} M NaClO_4 . As noted previously,⁷ films on $\text{CdCl}_2/\text{NaHCO}_3$ subphases are compressible to small areas ($< 20 \text{ \AA}^2/\text{molecule}$), although we have verified that, when IV is hydrolyzed by spreading on 0.1 M NaOH, the residual film has the characteristics of a stoichiometric amount of octadecanol (i.e., requires an area of $21 \text{ \AA}^2/\text{molecule}$).

Optical Spectroscopy of Glass Supported Monolayers. Pure monolayers of III and IV as well as mixed monolayers of I with III, IV, *n*-octadecanol, and cadmium arachidate, have been transferred to hydrophilic glass slides with good deposition ratios (1.0 ± 0.1). Monolayers formed from mixtures of Ia with cadmium arachidate (1:9 molar ratio in the spreading solution) have been built into multilayer assemblies but possess 25–40% less absorption than expected ($\lambda_{\text{max}}^{\text{nm}}$, OD (20 layers), OD (2 layers)): 495, 1.7×10^{-2} , 2.3×10^{-3} ; 440, 2.6×10^{-2} , 4.3×10^{-3} . The absorption spectra of pure III and IV as monolayers on acid and base washed glass are shown in comparison with their solutions in 20% aqueous THF in Figure 8. The monolayer absorption spectra of mixtures of Ia (37 mol %) + IV (55 mol %) + octadecanol (8 mol %) and Ia (9 mol %) + III (55 mol %) + octadecanol (36 mol %) are similar to that of the pure components (Figure 9 in supplementary material).

While the emission from films of Ia and IV (from 10^{-3} M NaClO, subphase, pH ~ 6) are identical (λ_{max} 685–690 nm), the intensity of III is twofold greater and appears slightly blue shifted to 680 nm. The two mixtures noted previously (from $\text{CdCl}_2/\text{NaHCO}_3$, pH 6.8) have broad emission maxima at 685–700 nm with intensity comparison uncertain owing to differences in film age. Immersion of any of these coated slides into distilled H_2O led to $\sim 50\%$ intensity decrease which did

not increase upon drying (vacuum desiccator, 15 h, <1 Torr at 35 °C).

Photolysis of Mixed Monolayers Containing I, III, and Octadecanol. Monolayers containing 86 mol % III, 5 mol % I, and 9 mol % octadecanol were transferred from 10^{-3} M NaClO₄ onto hydrophilic glass and irradiated with "white" light ($300 < \lambda < 900$ nm) for 60 min in contact with either 10^{-3} M HCl or 10^{-3} M HClO₄, both containing 10^{-1} M 2-propanol. HPLC analysis of the films desorbed from slides in the standard manner gave the following mole percent recovery for III (based on 3.8×10^{-9} mol originally transferred to the slide): photolyzed slides, 61–63%; dark, wet control, 63–71%; and dark, dry control, 82–89%. The disappearance quantum yield for III is $4 \pm 1 \times 10^{-6}$. No molecular hydrogen was observed; if any was produced $\Phi_{H_2} \lesssim 1 \times 10^{-4}$.

Discussion

Purity Considerations for Surfactant Ester Derivatives.

Obtaining well-defined pure preparations of these complexes requires considerable attention to detail. Our results indicate, furthermore, that manipulations such as are involved in the construction of monolayer assemblies can lead to degradation. Because of the subtlety of spectral changes associated with these chemical alterations, more specific analytical methods such as liquid chromatography must be employed to permit unambiguous characterization.⁹ While we have shown that these techniques suffice to quantitate the surfactant ions, our results demonstrate that it will also be necessary to measure and control the distribution of small counterions associated with the films to provide an adequate characterization of monolayer assemblies, because of the substantial effect of these counterions on their photophysics (and presumably photochemistry). On the other hand, monolayer techniques can provide confirmatory analytical information; thus the demonstration that final π - A curves of films which have been completely hydrolyzed are quantitatively identical with those for stoichiometric amounts of octadecanol distinguishes clearly between the di- and mono-octadecyl esters and offers additional evidence for the purity of our preparations.

Surface Pressure and Potential. In addition to their possible photochemical interest, monolayers of those complexes are novel because they represent the first example known to us of surfactant ions bearing double charges. Although their molecular areas are approximately twice as large, the ruthenium surfactants have π - A curves similar in shape to and showing the same counterion specificity as those of such singly charged cationic surfactants as docosyltrimethylammonium bromide (DCTAB). Monolayers of the latter compound, which have been studied extensively by Goddard, Kao, and Kung,²⁴ also exhibit a progressive contraction in area and decrease in compressibility as the counterion is changed in the sequence F⁻, Cl⁻, -Br⁻, -I⁻, -SCN⁻; their surface potentials decrease in the same order. As Goddard et al. pointed out, there is no adequate theory to account for these specific ion effects. Our results with polyvalent anions (Figure 2b) imply that electrostatic considerations alone are inadequate to predict the direction or magnitude of these condensing effects. While the approximately twofold difference in molecular area observed in comparing monolayers of I and the single-chain DCTAB might be rationalized as resulting from the presence of two octadecyl chains in I, the large areas observed for the single chain complexes III and IV are not consistent with this idea (Figure 7).

The extreme sensitivity of these monolayers to small concentrations of more strongly interacting ions also parallels the behavior of the long-chain quaternary compound; Goddard et al. found that 2×10^{-6} M SCN⁻ had as large an effect as 2×10^{-3} M Cl⁻ on the π - A curve of DCTAB when each was

added to 0.01 M NaF subphases. A similar high selectivity, with the same anion sequence, has also recently been reported for monolayers of cationic polymers.²⁵

We find substantial deviations from additivity in mixed films. Goodrich²⁶ also reported negative deviations from additivity of molecular area in monolayers containing charged surfactant and fatty alcohols; Davies and Rideal²⁷ suggested that these result from screening of repulsion between the charged groups. In view of the failure of simple electrostatic models to account for the properties of our single component films, the importance of this contribution in the mixed layers remains uncertain.

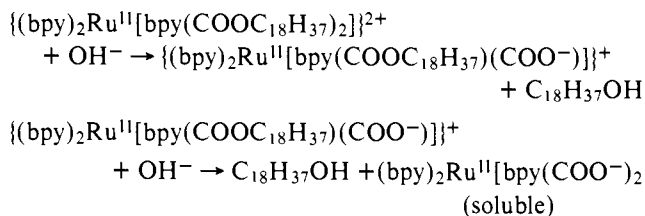
In the case of compound III, further complexity may be expected because of the unesterified carboxyl group. On neutral salt solutions (and perhaps even on 0.1 M HCl; vide infra), III may be expected to be extensively ionized.^{7,28} To a first approximation, the film may be considered as being composed of monocations, but it is likely that both positive and negative counterion specificities exist. While we have made no extensive examination of films of III and IV, or mixtures containing them, the very small areas to which these films are compressible on CdCl₂/NaHCO₃ subphases suggests that certain subphase compositions induce film collapse or the formation of unspread aggregates or dissolution.

In summary, it appears that variations in pH, subphase counterion content, and possible spreading artifacts must all be taken into account, and further study of surfactant component interactions with all of these variables controlled must precede any detailed interpretation of monolayer properties of mixed ruthenium complex surfactants.

Hydrolysis. A quantitative analysis of the progress of hydrolysis of I in spread monolayers is complicated by these same factors. The hydrolysis of V in aqueous solution at pH 10 is 50% complete (in terms of the final products) in about 45 min (Figure 3). For Ia in a mixture of 50% THF and 50% aqueous pH 10 buffer, the same extent of reaction requires ~9 min, while in the monolayer on pH 10 subphase it is still more rapid. The latter behavior must result from the increase in OH⁻ concentration near the surface induced by the positively charged surface layer.²⁹ We may write

$$pH_{\text{surf}} = pH_{\text{bulk}} + \frac{e\Psi}{2.3kT}$$

and approximate Ψ using the Davies equation, which leads to an expected increase of 4.0–4.6 units in the pH at the surface for monolayers of doubly charged ions occupying 150–85 Å²/molecule, on 10^{-3} M salt solutions. Clearly such large pH increments can account qualitatively for the observed rate enhancements. (They also provide the rationale for our earlier remark that the carboxyl group of IV in a monolayer might be ionized even at a bulk pH of 1, since these carboxyl groups appear to have $pK_a \sim 5.5$.²⁸ On the other hand, as the sequential hydrolysis reactions



proceed, the surface charge density is decreasing, and diffusion of the soluble ruthenium carboxylate away from the surface may be involved in the overall kinetics. Hence, the reaction rate expressions will be complex; in order to interpret film area changes, the nonadditivity of molecular area in mixtures will also have to be taken into account.

While we have no direct evidence, the enhanced rate of hy-

drololysis of I in 50% aqueous THF as compared with V in solution suggests aggregation of the surfactant in this medium. This would also account for the apparently decreasing rate as the reaction proceeds, since the charge on the micelles would progressively decrease just as in the case of the monolayer.

Luminescence of Monolayers on Aqueous Subphases. The most striking effect of counterions is their major influence on monolayer luminescence. Such differences are not found in homogeneous solution; the addition of 1 M solutions (20 vol. %) of KF, KCl, KBr, KNO₃, KOAc, NaClO₄, NaBF₄, or KSCN to Ia in THF solution leads to no more than 20% change in the observed emission intensity, as compared with the same concentration (5.2×10^{-5} M) of Ia in 20% aqueous THF; a substantial (80%) decrease in emission is observed on addition of 1 M KI. Similarly, the emission intensity of II and V in aqueous solution is unaffected by addition of 1 M salts (including KI, and also KCl or NaClO₄ at the level of 4 M).

We are unable to estimate the quantum yield of luminescence in the monolayer fluorimeter; so it is not possible to decide whether the difference in luminescence intensity results from a reduction in yield by ions such as Cl⁻, or an enhancement by ClO₄⁻, as compared with yields in other environments. The large solvent effects on luminescence yield of Ru(bpy)₃²⁺ derivatives^{12,22,30} suggest that the environment change induced by interaction with the strongly condensing ClO₄⁻ ions might enhance luminescence. Another case of anion alteration (increased lifetime, reduced nonradiative decay rate) of luminescence properties for a transition metal bipyridyl complex has recently been reported,³¹ although, since in that instance a different type of excited state is affected and the effect is observed in aqueous solution, the observations may be unrelated.

Förster theory calculations based on the small overlap between absorption and emission spectra of I in CHCl₃ solution (using a luminescence quantum yield, $\Phi_L = 0.18$ ³²) leads to an energy transfer distance, $R_0 = 15$ Å. (If we attempt to correct this value for the monolayer environment by introducing $\Phi_L = 0.045$, as measured for aqueous solutions of the dimethyl ester,³⁰ we obtain $R_0 = 12$ Å). In a close-packed array occupying 85 Å²/molecule, the center-to-center distance is 10.1 Å. Hence, we might expect that a substantial amount of energy migration could occur in these films. Nevertheless there seems to be no evidence of concentration quenching as the chromophores are brought closer together in monolayers on chloride subphases (Figure 4).

Monolayers on Glass Slides. The deposition of a single monolayer of I on withdrawing a hydrophilic (prepared by sonication in Alconox) glass slide from subphases of H₂O, NaCl, or CdCl₂/NaHCO₃ at $\pi = 30$ dyn/cm appears to proceed smoothly. Unit deposition ratios, reproducible absorption spectra, and quantitative recovery of unchanged I on subsequent extraction have been demonstrated repeatedly. Variants in procedure, however, lead to artifacts. Films transferred from 10⁻³ M NaClO₄ subphases have yielded anomalously high recovery on extraction even though film deposition ratios were unity, the most probable interpretation is formation of some patches of unspread material near the partially immersed slide during spreading on this subphase. We have also observed unspread material resulting from attempts to spread to high surface density on this subphase. Monolayers deposited on top of cadmium arachidate layers have diminished optical absorption, and we have been unable to demonstrate quantitative recovery of the monolayer-forming material; as noted above, it is not clear whether this results from an artifact in the analysis.

The pretreatment of the glass affects the monolayers deposited on it. As Table I shows, monolayer coated slides pretreated with reagents such as NH₄HF₂ and stored without exposure to water exhibit hydrolysis of I. On subsequent ex-

posure to liquid water, further hydrolysis is very dependent on slide pretreatment.

It is known that the pH of the solution will increase upon soaking soda lime glass (such as the microscope slides used here) in distilled H₂O.³³ We could then expect that the base-catalyzed hydrolysis reaction could be minimized either by producing an acidic hydrated surface layer on the substrate or by retarding the solubilization and/or diffusion of the alkaline components out of the bulk substrate. In the present work, this result seems to have been achieved by sonicating the soda-lime glass in an alkaline detergent (Alconox); the monolayer absorption spectrum of III on such a pretreated surface shows the protonated rather than ionized carboxylic acid group (Figure 8). To a lesser extent, this result is also realized by employing hydrophobic glass surfaces (Me₂SiCl₂ treatment) covered with five layers of cadmium arachidate. Such a surface preparation decreases the amount of I hydrolyzed to III by a factor of three from acid-washed slides.

Glass surfaces are known to exhibit cation-exchange properties;³⁴ whether anions may also be adsorbed seems less certain. However, the counterion distribution may well change during the process of monolayer transfer; even if the glass surface does not specifically bind anions, there is evidence from studies of fatty acid soap films that the counterion distribution in deposited layers may differ from that existing in the monolayer on the aqueous subphase.³⁵ Ion redistribution, furthermore, may be time dependent.³⁶

While we have not examined these processes in detail, it seems likely that much of the variability in luminescence from deposited ruthenium complex layers observed by us and others¹⁸ arises from variations in counterion incorporation.

Photolysis of Monolayer Assemblies. The observation of the photochemical cleavage of water by monolayer bound derivatives of Ru^{II}(bpy)₃²⁺ appears limited to a single preparation.⁸ All experimentation using subsequent preparations, including those contained herein, has failed to confirm that observation.^{8,22,30} In an attempt to understand what the unique nature of that original monolayer film might have been, we will compare our few direct observations on the original preparation³⁷ (both as a solid and as monolayers on cadmium arachidate/glass), kindly supplied by Professor D. G. Whitten, with those of our own preparations and the literature.^{8,22,30}

HPLC analysis of the original preparation gave the following composition before and after washing a CHCl₃ solution with H₂O (relative percent, before (after)): 28 (0), Ru(COOR)₂; 36 (55), Ru(COOC₁₈)(COOR); 3 (4), Ru(COOC₁₈)(COOC₁₆); and 30 (35), Ru(COOC₁₈)₂ (where R ≡ H or Et).³⁸ The resolution of the column used for this particular analysis was not sufficient to separate Ru(COOC₁₈)(COOH) and Ru(COOC₁₈)(COOEt). However, the emission spectrum of the solid residue left after evaporation of the water-washed CHCl₃ solution in 20% aqueous THF showed a maximum at 720 nm (corrected) which underwent slight change (10% intensity decrease and 5-nm red shift) upon acidification. Based upon our observations of the emission spectra III and IV in 20% THF, we assigned R ≡ Et in Ru(COOC₁₈)(COOR). The water-soluble component was not analyzed in this manner and the total sample amount was too small to permit HPLC detection of octadecanol if any was present.

The absorption spectrum of a slide received by us already coated with a monolayer of the original material on six layers of cadmium arachidate showed ($\lambda_{\text{max}}^{\text{nm}}$, OD $\times 10^3$ (2 layers Ru complex)): 485, 7.4; 424, 8.4; 400, 7.6. The uncorrected emission spectrum of a precoated slide had its maximum at 670 nm, the same wavelength observed for CHCl₃ solutions of I and IV on our spectrometer but at 20–25-nm shorter wavelength than noted for monolayer assemblies of either I or IV. No intensity comparisons could be made owing to different

slide geometries and the sensitivity of the emission to sample placement. The emission of the precoated slide was quenched 40% upon immersion into distilled H₂O. After extended irradiation (100-W Hg lamp, 1000 h) in contact with H₂O, no emission was observed. HPLC analysis of material incompletely recovered (only ~4 mol % total recovery obtained by soaking slides in pure THF) from several precoated slides gave the following relative percent composition: 29, Ru(COOC₁₈)-(COOR); 6, Ru(COOC₁₈)(COOC₁₆); 65, Ru(COOC₁₈)₂ (where R is either H or Et and cannot be specified).

While I requires a molecular area of ~85 Å² (at 30 dyn/cm; see Figure 2a), we have obtained a mixture of I (37 mol %), IV (55 mol %), and *n*-octadecanol (8 mol %) which closely matches the full π -*A* curve reported⁸ for the original preparation and its ruthenium surfactant composition (octadecanol unknown). However, the monolayer absorption spectrum on hydrophilic glass from a film spread on CdCl₂/NaHCO₃ differs ($\lambda_{\text{max}}^{\text{nm}}$, OD $\times 10^3$ (2 layers ruthenium complex): 500, 4.2, 430, 6.4; ~405, 6.4) from that of the original preparation and the monolayer emission spectrum is identical with that of pure I (same film age). Note that a monolayer of the original preparation has ~40-fold greater emission intensity and 15–20-nm shorter wavelength maxima than I.⁸ While both a small increase in emission intensity (ca. twofold) and a blue shift of the maximum (~10 nm) can be expected by spreading the mixed film on a subphase containing NaClO₄ rather than CdCl₂/NaHCO₃ before transfer to glass by analogy to pure I and IV, the condensing effect of the ClO₄⁻ counterion on the positively charged film will certainly change the π -*A* curve. Hence, such a mixture of I, IV, and octadecanol does not provide the crucial composition by these criteria.

Although monolayers of pure III transferred to hydrophilic glass from 10⁻³ M NaClO₄ show an emission maximum (680 nm, uncorrected) close to that of the original preparation, the intensity is only twice that observed for I under the same conditions and the π -*A* curve is condensed (see Figure 7). The properties of a mixed monolayer film of I (9 mol %), III (55 mol %), and octadecanol (36 mol %) described in the Results section also do not match well with those of the original preparations.

In no case have we observed complete quenching of the luminescence upon immersing a monolayer coated slide into distilled H₂O or that it is recoverable upon heating under vacuum as reported previously.⁸ The largest emission intensity decreases (80%), irrespective of monolayer composition, were noted for those films transferred from aqueous NaClO₄ subphases. The only manner in which the intensity was subsequently recovered, and then only partially, required the addition of 1 M NaClO₄ to the aqueous solution contacting the glass-bound monolayer during the emission measurement.

In no case have we observed gas bubbles or subsaturation concentrations of molecular hydrogen upon irradiation of pure components or mixtures, $\Phi_{\text{H}_2} \leq 10^{-4}$. The sensitivity did not allow stoichiometric detection of H₂, but was sufficient to have found ten H₂ molecules per molecule of adsorbed ruthenium complex. The conditions of acidity and added hydrogen atom donor, 2-propanol, were those under which the 254-nm irradiation of Fe^{II}(CN)₆⁻⁴ has produced molecular hydrogen ($\Phi_{\text{H}_2} = 0.43$).⁴⁰ The choice of Cl⁻ or ClO₄⁻ as counterion in the photolyte had no effect. Neither Harriman³⁰ nor Seefeld et al.²² have detected water splitting by monolayers of Ru(COOC₁₈)₂ on slides.

Although we have seen the disappearance of I (or III) to unknown products during the course of an irradiation ($-\Phi \sim 5 \times 10^{-6}$), in no case have we observed the formation of III (or IV) via photohydrolysis as previously reported.⁸

The data of Table II show that the amount of III produced from I in the irradiated (1–2 h) slides is always within 2% of that found in the dark, aqueous control. Since this dark hy-

drolysis reaction is important over long irradiation periods, it is not surprising that ultimately no surfactant ruthenium complex would remain on the slides even in the absence of irreversible photochemical reactions. While both Sprintschnik et al.⁸ and Seefeld et al.²² have observed loss of the ruthenium complex from slides during long-term photolysis in water, neither group has given quantitative data on the rate of dark hydrolysis under similar conditions. Our results indicate that (at least for our slides) this process, while it does contribute to loss (either in the dark or light), must be supplemented by other photochemical degradation processes in long-term photolyses.

In view of the failure of these compounds to catalyze the photodecomposition of water in our experiments, and the complexity introduced by their instability to hydrolysis, we have turned our attention to the hydrolytically stable surfactant complex {(bpy)₂Ru^{II}[bpy(C₁₉H₃₉)₂]}²⁺, which we have synthesized. In future work with this compound, we plan to examine further the effect of counterions on the photophysics in monomolecular layers, as well as extending these studies to examining light-induced electron-transfer reactions.

Acknowledgments. The authors thank M. Calvin, J. E. Hallgren, L. Interrante, G. Porter, and M. Wrighton for helpful discussions leading to the preparation of this report and to D. G. Whitten for transmittal of experimental results and samples of Ru(COOC₁₈)₂. This work was partially supported by the Division of Basic Energy Sciences, DoE (EG-77-C-02-4395) and the National Science Foundation (AER75-01577).

Supplementary Material Available: Details of synthesis and characterization of compounds I–V, results of dark hydrolysis of glass supported monolayers of Ia (Table I), and absorption spectra of monolayers of mixtures (Figure 9) (9 pages). Ordering information is given on any current masthead page.

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Hydrogen Bonding of Water to Gas-Phase Ions. Structural and Stereochemical Effects in Protonated Phenols

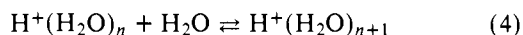
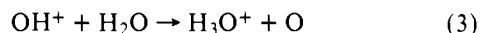
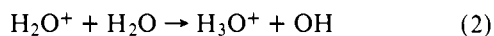
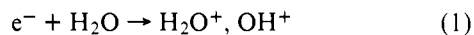
D. P. Martinsen and S. E. Buttrill, Jr. *¹

Contribution from the Department of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455. Received September 12, 1977

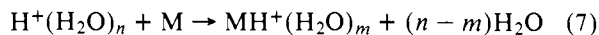
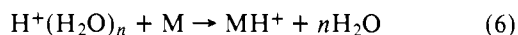
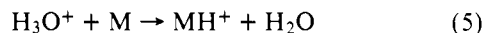
Abstract: The water chemical ionization mass spectra of substituted phenols M contain, in addition to the expected MH⁺ ions, hydrogen-bonded clusters of the protonated phenol with water, MH⁺·(H₂O)_n (n = 1–3). The relative intensities of these ions obtained at 120 °C and 0.3 Torr H₂O in a conventional ion source show significant differences which make it possible in most cases to distinguish ortho, meta, and para isomers. Using a new pulsed high-pressure source, equilibrium constants and ΔG at 450 K were measured for the reaction MH⁺ + H₂O ⇌ MH⁺·H₂O for 17 phenols. The excellent correlation between ΔG⁴⁵⁰ and the ratio of MH⁺·H₂O to MH⁺ in the conventional water CI spectra indicates that equilibrium, rather than kinetic effects, governs the relative intensities of these ions under CI conditions. Gas-phase hydrogen bond strengths are a sensitive new probe of the structure and intramolecular interactions of protonated molecules.

Introduction

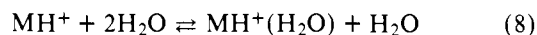
In chemical ionization mass spectrometry,² the initial ionization, usually induced by high-energy electrons, occurs in a reagent gas present at pressures of 0.1–10 Torr in the mass spectrometer ion source. Although methane and isobutane are the most common reagent gases, we have used water extensively for the last few years.^{3–7} The most important processes leading to the formation of the stable reagent ions in water⁸ are summarized in the reactions



The reactions of the hydronium ion and its hydrates with the sample molecules produce ions characteristic of the sample,



In addition to these bimolecular processes (eq 5–7), the protonated sample may also form a hydrogen-bonded cluster with one or more water molecules through termolecular reactions.



These last reactions are readily reversible and under appropriate conditions can lead to the establishment of thermo-

chemical equilibrium among all or some of the ionic species present in the mass spectrometer ion source.^{8,9}

One of our first observations regarding water CI spectra was that the relative intensities of the MH⁺ and the MH⁺(H₂O)_n ions seemed to depend very much on the functional group protonated. When instrumental parameters, such as source temperature and pressure, are carefully controlled, these peaks provide analytically useful information on the structure and stereochemistry of the sample.⁶ In order to study the origins of these useful and interesting effects, we have constructed a pulsed high-pressure ion source which enables us to monitor the time dependence of the ion concentrations and obtain both kinetic and thermochemical information about the formation of the hydrogen-bonded cluster ions. This paper reports our results from both conventional and pulsed high-pressure water chemical ionization mass spectrometry for some substituted phenols.

Experimental Section

The modifications to our Du Pont 21-490B mass spectrometer for conventional chemical ionization work have been described in previous publications.^{3,5,7}

The new pulsed high-pressure source is shown in Figure 1. All parts are stainless steel except for the insulator ring, which is made of Macor machinable glass ceramic.¹⁰ The shapes of the source block and source mounting plate are such that the insulator ring is shielded from the ions, electrons, and reactive species generated within the ion source. A potential difference of up to 12 V may be applied between the source block and mounting plate if necessary to extract the ions. For these experiments, this voltage was kept below 0.5 V.

Because of their critical importance in determining equilibrium thermodynamic properties of ions, special provisions were made for accurately measuring the temperature and pressure in the source. The source block is equipped with two heater wells extending the full width