cymene to the partially anionic (and basic) ketyl.

After statistical correction, primary protons are seen to be 1.1 times as reactive as tertiary protons in the chemical decay of this exciplex, in total disregard for C–H bond strengths. It might be concluded that all selectivity has vanished, but further work is required before that generalization can be justified. In fact, any competitive direct hydrogen atom abstraction by triplet ketone would *raise* the observed P/T ratio. We estimated a maximum rate constant of 1×10^6 M^{-1} s^{-1} for direct H abstraction from cumene by triplet AF_3.[1] Since p-alkyl groups increase reactivities by a factor of three,[1,5] we estimate a maximum of 3% direct H abstraction from p-cymene. Correction for this small percentage raises the exciplex-derived P/T to 3.7, 1.2 per proton.

What seems most remarkable is that the 10-fold change in selectivity, in the direction opposed to bond strengths, results from only a small fraction (~20%) of electron transfer[1,7] in the triplet exciplex. It is difficult to find results with which to compare these. Cohen observed that methyl groups of dimethylbutylamine are preferentially photooxidized by ketones in alkaline aqueous media.[2,8] Co(III) catalyzed oxidation of p-cymene in acetic acid, a process which has been interpreted to involve the aromatic radical cation,[9] gives products resulting from a 19:1 ratio of P/T radical formation.[10] Therefore, our much lower 3.4–3.7 ratio might be due to the partial rather than full positive charge on the H being abstracted. However, the presence of chloride ions reverses the Co(III) selectivity to 1:3 P/T, more in line with the 1:2 P/T ratio observed in the electrochemical oxidation of cymene in methanol.[11] The relative acidities of protons in aromatic radical cations apparently are strongly solvent and base sensitive.

The photoreduction of dimethyl terephthalate by p-cymene, a reaction which probably involves substantial charge transfer,[12] has been reported to yield TT as the only hydrocarbon and cross-coupling products analogous primarily to KP![13] No clear-cut P/T ratio can be gleaned from this earlier study.

We are currently investigating the relative proton labilities of various other aromatic systems as well as the effects of external protons.[14]

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Peter J. Wagner,* Allen E. Puchalski
Chemistry Department, Michigan State University
East Lansing, Michigan 48824
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Structure of Reactively Produced Choropropene Cations by Laser Photodissociation

Sir:

The unambigous identification of reaction products by spectroscopic means is an indispensible tool of mechanistic investigation which has until very recently been denied to the gas-phase ion–molecule reaction investigator. This situation has been changed by the recent advent of the technique of photodissociation spectroscopy. By observing the extent of dissociation as a function of wavelength, a photodissociation spectrum of a cation can be obtained which reflects many of the same characteristics as its optical absorption spectrum. Over the past several years this technique has been utilized
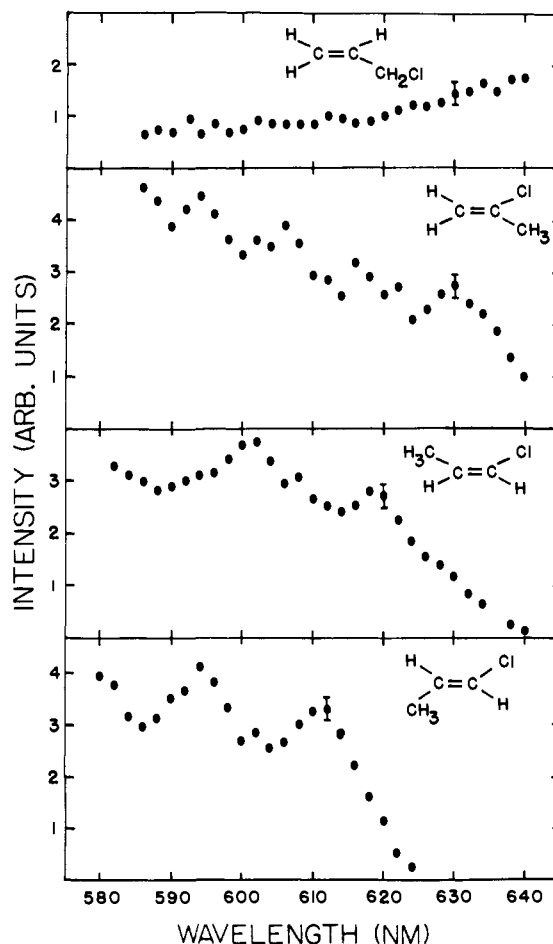
Figure 1. Laser photodissociation spectrum of the isomers of chloropropene cation from top to bottom: allyl chloride cation, 2-chloropropene cation, cis-1-chloropropene cation, and trans-1-chloropropene cation.
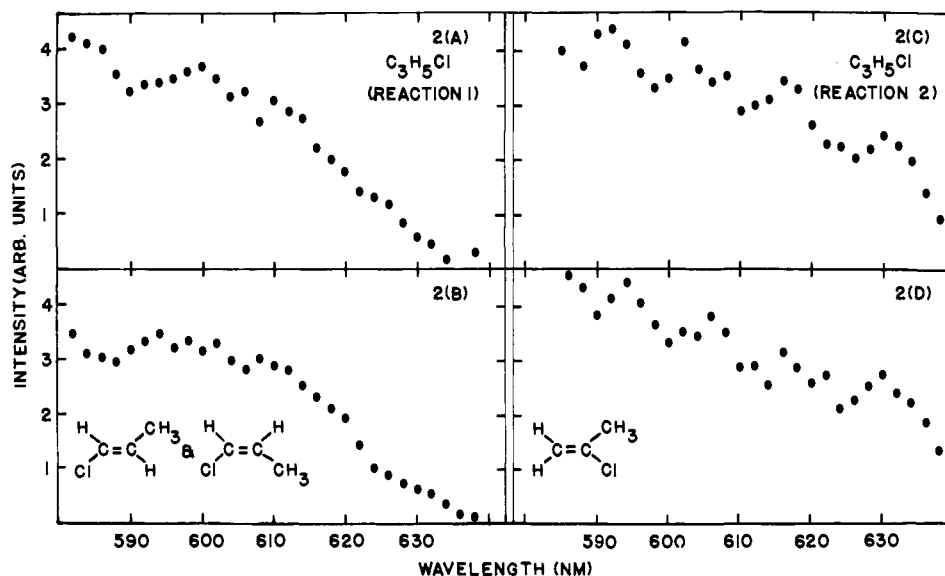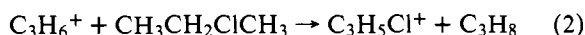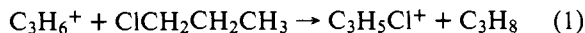
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Figure 2. (A) Laser photodissociation spectrum of $C_3H_5Cl^+$ formed in reaction 1. (B) The photodissociation curve for a mixture of *trans*- and *cis*-1-chloropropene cation as calculated from the results in Figure 1. (C) Laser photodissociation of $C_3H_5Cl^+$ formed in reaction 2 which is compared with the spectrum for 2-chloropropene cation (D).

effectively in the spectroscopic structure investigation of isomeric cations.[1,2] Many of these spectroscopic investigations obtained the photodissociation spectrum with an optical resolution of 10–20 nm, which usually precludes resolution of vibrational structure within the photodissociation curve. Recently, with the use of tunable dye lasers, several workers have reported the observation of well resolved vibrational structure[3,4] of various cations which has resulted in important information about vibronic transitions and vibrational frequencies of the ions. We report here the laser photodissociation spectra of isomers of chloropropene in which there was observed resolved vibrational structure in the photodissociation spectrum. The characteristic spectra of the isomers were exploited in product-structure characterization of the product $C_3H_5Cl^+$ ions from reaction of $C_3H_6^+$ with 1-chloropropane and 2-chloropropane, clearly illustrating the value of such highly specific, vibrationally resolved spectra in ion structure analysis.

The spectra of the various isomers are shown in Figure 1. They were obtained with a pulsed-mode ion cyclotron resonance spectrometer with a tunable dye laser source which has been described,[3] operated with constant power output from 580 to 645 nm. The chloropropene ions were formed by electron impact of the neutral isomers with electron energies typically 1 eV above the IP of the molecule. The photodissociation ionic fragment was $C_3H_5^+$ for all isomeric ions.

As can be seen in Figure 1,[5] vibrational structure is observed for 2-chloropropene and 1- (*cis*- and *trans*-) chloropropene cations. The spectrum for allyl chloride cation, on the other hand, is distinctly different from the other curves, showing a decrease in the extent of dissociation at shorter wavelengths and lacking any resolved vibrational structure. The most striking distinction between the spectra of 2-chloropropene and 1- (*cis*- and *trans*-) chloropropene cations is the observed difference in the position of the 0–0 transition. The *trans*-1-chloropropene has the apparent 0–0 transition at 611 nm while the cis isomer is red shifted by ~8 to 619 nm. The 2-chloropropene is further red shifted to 630 nm and shows a clear vibrational progression spaced at 320 ± 20 cm^{-1}. It is clear from the differences in both the 0–0 transition and the observed vibrational structure that the four isomeric cations have independent and noninterconverting structures.

$C_3H_5Cl^+$ is formed by the following ion-molecule reactions:

$$C_3H_6^+ + ClCH_2CH_2CH_3 \rightarrow C_3H_5Cl^+ + C_3H_8 \quad (1)$$

$$C_3H_6^+ + CH_3CH_2ClCH_3 \rightarrow C_3H_5Cl^+ + C_3H_8 \quad (2)$$

A reaction analogous to reactions 1 and 2 was observed previously in the study of the ion–molecule reactions of ethyl chloride where $C_2H_4^+$ upon reaction with the ethyl chloride neutral formed $C_2H_3Cl^+$.[6] To determine the structure of the $C_3H_5Cl^+$ formed in reactions 1 and 2 the laser photodissociation spectra of the product ions were taken, as shown in Figure 2. As can be seen in Figure 2(A), the photodissociation spectrum of the $C_3H_5Cl^+$ formed in reaction 1 shows little vibrational structure. The low extent of photodissociation observed at 630 nm and higher wavelengths rules out allyl chloride cation and 2-chloropropene cations as major product-ion components; the $C_3H_5Cl^+$ cations in reaction 1 and are probably composed of 1-chloropropene, with the loss of vibrational structure reflecting a mixture of *cis*- and *trans*-chloropropene cations. In Figure 2(B), the calculated photodissociation spectrum for an equal mixture of *cis*- and *trans*-chloropropene cations is shown. As can be seen the agreement is satisfactory, supporting the concentration that the $C_3H_5Cl^+$ is composed of a mixture of cis and trans isomers.[7]

The photodissociation spectrum of $C_3H_5Cl^+$ formed in reaction 2 is shown in Figure 2(C). The spectrum shows vibrational structure and a 0–0 transition at 630 nm. Shown in Figure 2(D) is the photodissociation spectra of 2-chloropropene. It is evident that there is good agreement in curve shape and cross section between the two curves in the region of the 0–0 transition, although at shorter wavelengths there are differences outside of experimental uncertainty. This comparison indicates that the major portions of the $C_3H_5Cl^+$ ions formed in reaction 2 have the 2-chloropropene structure, while there may be some 1-chloropropene present as well. For example, a mixture of 60% 2-chloropropene and 40% *cis*-1-chloropropene cation would satisfactorily reproduce the photodissociation spectrum observed for the $C_3H_5Cl^+$ produced in reaction 2.

A striking conclusion of this work is the retention of cis and trans identity of the 1-chloropropene ions. The very solidly based conclusions about the product-ion structures from reactions 1 and 2 point up the value of the resolved vibrational spectral structure in drawing conclusions about product-ion structures and reactions mechanisms. The definite nonidentity of the products of reactions 1 and 2 carries a strong implication

that the $C_3H_5Cl^+$ skeleton is derived from the neutral reactant, perhaps by formal H_2^- abstraction; a complementary isotope-labeling study will clearly be useful.

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Robert G. Orth,* Robert C. Dunbar

Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Luminescent Probes for Detergent Solutions. A Simple Procedure for Determination of the Mean Aggregation Number of Micelles

Sir:

One of the most fundamental and important structural parameters of micellar aggregates is the aggregation number, or the average number of detergent molecules in a micelle unit.[1] The measurement and establishment of aggregation numbers is therefore of great significance. We report here a simple procedure for measuring the mean aggregation numbers of detergent solutions. The method is based on the quenching of a luminescent probe by a hydrophobic quencher.

The mean aggregation number of micelles may be derived from luminescence quenching measurements if "static" or "active" sphere[2] quenching of a micellar donor by a micelle associated quencher is dominant. Suppose a solution contains a well-defined but unknown micelle concentration [M] and a macroscopic concentration of quencher [Q]. If Q is selected so that it resides exclusively in the micellar phase, then the molecules of Q will be distributed among the available micelles in some fashion. If a luminescent molecule D, which is also completely associated with micelles, is now added to the system, D will partition itself both among micelles contaning Q and among "empty" micelles. We select Poisson statistics to describe the distribution of D and Q among micelles in the tertiary system D, Q, M. If D is luminescent only when it occupies an empty micelle (i.e., D* is completely quenched when it occupies a micelle containing at least one Q), then the *measured* ratio of luminescence intensities $(I/I°)$ in the presence of Q to that in the absence of Q is related by the very simple expression

$$(I/I°) = \exp\{-[Q]/[M]\} \tag{1}$$

The simplicity of this expression derives from the assumption that only D* in micelles containing no Q emit.[3] This assumption can be tested experimentally since, as a function of increasing [Q], the luminescence lifetime should not change even though the luminescence intensity is decreased, i.e., "static" quenching occurs. [M] can be related to the measurable
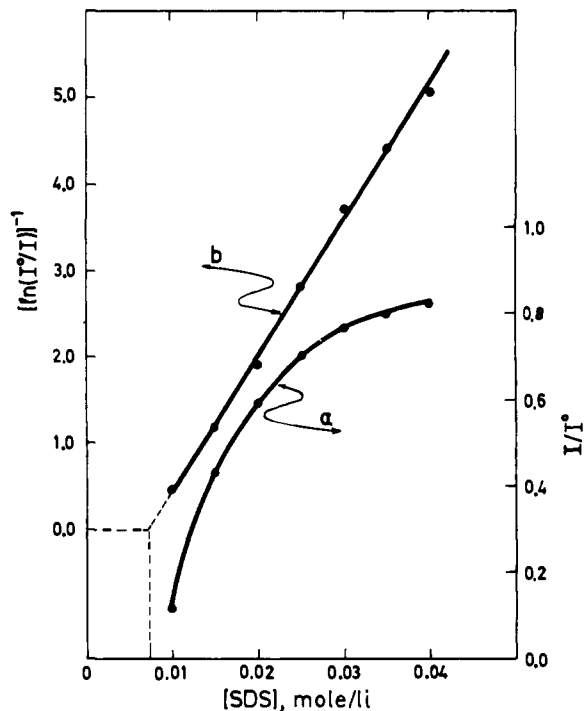
Figure 1. Detergent concentration dependence of 7.2×10^{-5} M, D = $Ru(bipy)_3^{2+}$ luminscence intensity. Q = 9-methlanthracene fixed at 1.05×10^{-4} M. Curve a: intensity normalized relative to that in the absence of Q. Curve b: analysis according to eq 3 of text. Excitation and emission wavelengths were at 450 and 630 nm, respectively (25 °C).

macroscopic concentration of detergent, [Det], and the mean aggregation number, $\bar{n}$, by the expression

$$[M] = \frac{[Det] - [free\ monomer]}{\bar{n}} \tag{2}$$

where the free monomer concentration in equilibrium with the micellar aggregates is almost equal to the critical micelle concentration, cmc. The combination of expression 1 and 2 leads to

$$\ln(I°/I) = \frac{[Q]\bar{n}}{[Det] - [free\ monomer]} \tag{3}$$

We are in a position to evaluate both the aggregation number, $\bar{n}$, and the concentration of free monomer in equilibrium with micelles by measuring $I°/I$ as a function of [Q] at fixed [Det] and by measuring $I°/I$ as a function of [Det] at fixed [Q].

The experimental system of this report uses luminescent donor D = $Ru(bipy)_3^{2+}$, luminescence quencher Q = 9-methylanthracene, and detergent = sodium dodecyl sulfate (SDS). The system meets the requirement of a water-insoluble quencher and micelle-associated donor.[4] Furthermore, several evaluations of the aggregation number of SDS have been reported in the literature as a function of experimental variables.[5-8]

At [D] ≤ 7.2×10^{-5} M, eq 1 is obeyed. Measurements of luminescence lifetime of D* yielded a constant value at 0.48 μs (±3%) *even under conditions where quenching had reduced the luminscence intensity by an order of magnitude.* Comparable quenching in a homogeneous solvent such as acetonitrile (no SDS) resulted in the expected (Stern-Volmer) decrease of both luminscence intensity and lifetime.[9]

To verify the functional form of eq 3, two sets of experiments were run, in each keeping one of the variables constant. Figure 1a shows the dependence of luminescence intensity keeping [Q] fixed at 1.05×10^{-4} M. The luminescence intensity *increases* as [SDS] is *increased.* This observation is readily explained by our model. Increased micelle concentration plays a protective role by keeping the donor and quencher molecules