

drogen atom abstraction.⁶ Growth curves of η vs. time are shown for CQ in Figure 2. The temporal dependence is quadratic as described by eq 1. In Figure 3, the quantity $a(I)$ which has been extracted from the growth curves is shown as a function of I . From the slope of this curve, one obtains a value of $n = 1.04$, indicating that the reaction is a linear single-photon process. The accuracy of the determination of n by this method is much greater than by the conventional method of following the decrease in the absorption intensity of the starting material.⁷ The uncertainty in values of n obtained by the holographic technique is 5% compared with 20% for the direct absorption method. The holographic technique has the additional advantage that only a tiny portion of each sample, i.e., the area of the focused laser beam (<0.5 mm²), is used for each measurement.

In summary, a simple new method of following the temporal course of a photochemical reaction has been described. The technique does not require sophisticated optics or electronics.

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Direct Cyanation of Aromatics

Sir:

We wish to report a method for the direct introduction of a cyano group onto aromatic rings. Since there are no general methods for direct cyanation,¹ this reaction may have synthetic utility. The results are of particular interest because they illustrate an unusual preparative approach—plasma chemistry.² Furthermore, the observed positional selectivity patterns, which include *ipso* substitution for all substituents examined, are exceptional and of considerable intrinsic interest.

The inductively coupled plasma apparatus is very similar to those previously described.^{3,4} Cyanogen (Matheson Co.) and the respective aromatic compound were codistilled through the discharge zone generated by a rf generator at 13.56 MHz. Products and unreacted starting materials were frozen out in a liquid nitrogen cooled trap and were analyzed by GLC. The products were identified by comparison with authentic samples and in most cases confirmed by GLC-MS. Yields were generally estimated by GLC with an internal standard.

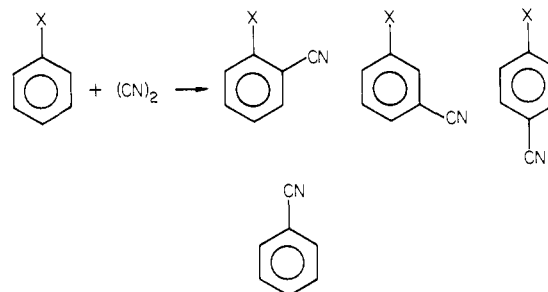
Consider first the conversion of benzene to benzonitrile. Under appropriate flow rate and power conditions, the yield of benzo-

Table I. Yields of Cyanoaromatics from C₆H₅X

X	pow- er, W	flow rate, mmol min ⁻¹		% yield ^b of phenyl derivative			
		r _A ^a	r _B ^a	<i>o</i> -X, CN	<i>m</i> -X, CN	<i>p</i> -X, CN	CN
H	45	4.3	2.9	1.9 ^c	2.8 ^c	1.7 ^c	94
CH ₃	70	5.8	3.2	26	21	13	11
CF ₃	48	2.1	2.0	11	32	9.1	6.0
OH	48	2.1	1.5	18	10	8.3	9.0
F	40	3.3	1.8	14	17	14	4.0
Cl	50	2.5	1.9	17	19	17	20
Br	60	2.6	1.7	5.3	6.2	4.2	9.2
N ^d	50	4.0	1.2	20	34	10	

^a r_A and r_B are flow rates of cyanogen and the respective aromatic compound. ^b Yields based on reacted aromatics and are representative of several runs. Conversion was ~70% of the cyanogen and ~50% of the aromatic. ^c Dicyanobenzenes. ^d Starting material is pyridine.

nitrile is 94% based upon the 45% benzene (8 g) which reacted during one pass. The yield based on reacted cyanogen is 64%. A wide variety of substituted benzenes (C₆H₅X, X = CH₃, CF₃, OH, F, Cl, Br) and pyridine are similarly cyanated, providing good yields of ortho, meta, para, and ipso-substituted products.



Typical yields are indicated in Table I. In these experiments the conversion of aromatic was typically 50% and the conversion of cyanogen was typically 70%. Only in the case of benzene were the yields optimized. Hydrogen cyanide was always found as a coproduct, and small amounts of dicyanoaromatics were also produced. These products were minimized by keeping the conversion of aromatic reactant less than 60%. In all reactions, not more than 0.5% biphenyl was found. For toluene, less than 0.2% benzyl cyanide from side-chain reaction was observed and about 5% bibenzyl was detected.

The utility of this reaction is limited by the unselectivity of substitution and the need to vaporize the aromatic.⁵ The advantages are that the reaction involves no heating, solvent or catalyst and a flow system. This is one of a very few cases in which two compounds have been used for a reaction in the plasma zone,⁴⁻⁷ and to our knowledge the only one which gives clean products for several substrates.

The observation that ipso substitution competes with substitution for hydrogen is unusual.⁸ The generality of ipso substitution is unprecedented, and especially remarkable is the displacement of fluoro. We suspect that the positional selectivity results from a very exothermic addition of cyano radical to the aromatic, followed by immediate loss of a hydrogen atom or the substituent, before the activated product can lose its energy by collisions. The mechanism, the origin of the selectivity, and other aspects will be elaborated in a future publication.

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Differential Quenching of Chromium(III) Photochemistry

Sir:

We report the observation of differential quenching of two reaction modes of a transition-metal complex, $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+$. The results are interpretable in terms of reaction of two different quartet excited states, and allow some quantitative analysis of the proportion of the two mechanisms and its wavelength dependence.

Wavelength and temperature dependencies of the ratio of reaction modes of mixed-ligand chromium(III) complexes have been reported^{1,2} and have been taken as indicating participation in photosolvation reactions by more than one excited state. Other possible mechanisms have been suggested, however, such as solvent-restricted relaxation³ and/or preferential selection of different solvent environments.⁴

Various approaches have been tried to identify the participating states. Fundamental studies of the emission and absorption properties of the excited states have been important, as has the use of sensitizers and quenchers. Sensitization studies have been somewhat disappointing since the results often parallel the direct photochemistry, exceptions being studies^{5,6} of $[\text{Cr}(\text{NH}_3)_5\text{NCS}]^{2+}$ and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ where different sensitizers were found to give differing NH_3/X ratios. The apparent lack of spin restrictions on the sensitizer/complex energy transfer has, however, unfortunately blurred the interpretation of such studies.

Quenching experiments have tended to be more definitive.⁷ For a number of complexes exhibiting a single reaction mode, it has been found possible⁸ to quench the phosphorescence more than the photochemistry, showing that at least part of the reaction occurs in competition with intersystem crossing to the thermally equilibrated doublet state. Whether the quenchable reaction occurs directly from the doublet or via back-intersystem crossing is still under active investigation, and it may transpire that both have been demonstrated for particular molecules.⁹⁻¹¹

The extension of such studies to the limited number of molecules which show more than one significant reaction mode offers the hope of gaining additional information from the possible effect of quenching on the reaction mode ratio. An investigation¹¹ of $t\text{-}[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$ revealed that the two reaction modes of this complex were quenched in parallel.

The molecule $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+$ photoaquates thiocyanate and ethylenediamine (one end) with a wavelength- and tempera-

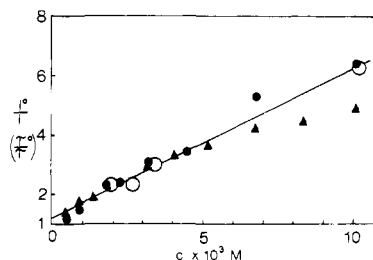


Figure 1. Emission intensity and lifetime quenching. $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+ = 4.02 \times 10^{-2} \text{ M}$, $1.02 \times 10^{-3} \text{ M HClO}_4$, $[\text{Cr}(\text{CN})_6]^{3-} = C \text{ M}$, $t = 5^\circ \text{C}$. Intensity quenching for 546-nm (●) and 436-nm (▲) excitation, corrected for quencher absorbance by Beer's Law. Lifetime quenching for 530-nm (○) excitation. By exclusion of the three high concentration points at 436 nm and giving double weight to the origin, the combined intensity data give a least-squares Stern-Volmer line $I^0/I = 1.03 + 614C$ to which the lifetime data fit well, as shown.

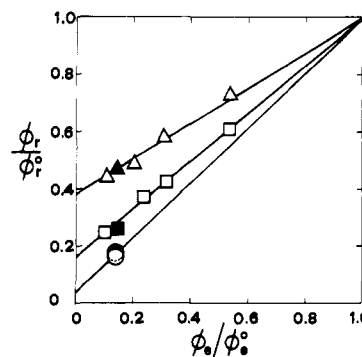


Figure 2. Reaction quenching vs. emission quenching. *Thiocyanate mode:* $\phi^0 = 0.256$ (546 nm) and 0.268 (436 nm).^{12,21} The quenching results plotted for excitation at 546 nm (●) and 436 nm (○) are each based on three quantum yield determinations with and without quencher, with $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+ = 4.0 \times 10^{-2} \text{ M}$ in $1.02 \times 10^{-3} \text{ M HClO}_4$, $[\text{Cr}(\text{CN})_6]^{3-} = 1.0 \times 10^{-2} \text{ M}$, $t = 10^\circ \text{C}$. *Ethylenediamine mode:* $\phi^0 = 0.068$ (546 nm) and 0.105 (436 nm).^{12,21} Points for 546 nm (□) and for 436 nm (▲) are single determinations except for the filled points which are the averages of two determinations. Concentrations as before except for variable $[\text{Cr}(\text{CN})_6]^{3-}$, $t = 5^\circ \text{C}$.

ture-dependent ratio.¹² It also emits¹³ at 717 nm from aqueous solution with quantum yield 10^{-4} at 22°C , and the emission is quenchable by $[\text{Cr}(\text{CN})_6]^{3-}$ and, less efficiently, by $[\text{Cr}(\text{ox})_3]^{3-}$. For excitation at 5°C and 546 nm, where quencher absorption is negligible, the linear Stern-Volmer plot for quenching of the emission intensity is shown in Figure 1. Excitation at 436 nm, where corrections for quencher absorption ranging up to 7% were necessary, yielded data in general agreement although some curvature in the plot is seen. This might be due to uncorrected errors (such nonlinearity could be caused by a few percent of scatter), but certainly for the lower concentrations of quencher excellent agreement was obtained for excitation at the two wavelengths. The least-squares line for the combined data set of Figure 1 yielded a slope of $614 \text{ L mol}^{-1} (5^\circ \text{C})$.

The decay lifetime of the emission at 6°C was observed by laser flash techniques¹⁴ to be $1.05 \mu\text{s}$, and the lifetime was quenched by $[\text{Cr}(\text{CN})_6]^{3-}$ with the same Stern-Volmer behavior as the intensity (open points in Figure 1). The excellent agreement between the two sets of measurements shows that the quenching is a collisional process. The lifetime and the Stern-Volmer constant together yield a quenching rate constant of $5.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, of the order measured for other systems⁷ involving dynamic quenching between transition-metal complexes. Thus, we have no reason to suspect any anomalies in the quenching by $[\text{Cr}(\text{CN})_6]^{3-}$.

Quantum yields for thiocyanate and ethylenediamine release with and without quencher were measured as before,¹² except for

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