Table I. Asymmetric Michael Addition of 2-Cyanopropionates **1** with **2** Catalyzed by the Rhodium Complex with (S,S)-(R,R)-TRAP (Scheme I)[a]

						product (**3–9**)			
entry	**2**, R^2	**1**, R^1	temp, °C	addition time, h[b]	time, h[c]	yield, %[d]	ee, %[e]	config[f]	$[\alpha]^{20}_{D}$, deg[g]
1	Me (**2a**)	Me (**1a**)	5	*i*	10	99 (**3a**)	72	*R*	+2.6
2	Me (**2a**)	Et (**1b**)	5	*i*	10	95 (**3b**)	81	*R*	+4.0
3	Me (**2a**)	*i*-Pr (**1c**)	5	*i*	10	99 (**3c**)	84	*R*[l]	+4.4
4	Me (**2a**)	*i*-Pr (**1c**)	3	*i*	10	97 (**3c**)	86	*R*[l]	+4.5
5	Me (**2a**)	*t*-Bu (**1d**)	5	*i*	10	95 (**3d**)	81	*R*	+2.7
6	Et (**2b**)	*i*-Pr (**1c**)	3	*i*	10	98 (**4**)	85	*R*	+4.5
7	Ph (**2c**)	*i*-Pr (**1c**)	5	1.5	2	95 (**5**)[j]	83[k]	*R*	+6.4
8	4-MeOPh (**2d**)	*i*-Pr (**1c**)	3	1.5	2	99 (**6**)[j]	89[k]	*R*	+5.4
9	2-MeOPh (**2e**)	*i*-Pr (**1c**)	3	1.5	2.5	98 (**7**)[j]	86[k]	*R*	+0.79[m]
10	4-ClPh (**2f**)	*i*-Pr (**1c**)	3	4	4.5	98 (**8**)[j]	85[k]	*R*	+6.7
11	H (**2g**)	*i*-Pr (**1c**)	3	2.5	3.5	88 (**9**)[j]	87	*R*	+3.1
12[h]	H (**2g**)	*i*-Pr (**1c**)	3	6	7	89 (**9**)	84	*R*	+3.1

[a] **1**/**2**/RhH(CO)(PPh$_3$)$_3$/TRAP = 100/150/1/1.1 unless otherwise noted. [b] Solution of **2** in benzene was added to a mixture of **1** and the catalyst over a given period. [c] Reaction time including the addition time. [d] Isolated yield by bulb-to-bulb distillation unless otherwise noted. [e] Determined by GLC analysis of the cyano ester with chiral capillary column Chiraldex G-TA (0.25 mm × 30 m, base line separation) unless otherwise noted. [f] Determined by the chemical correlation with (R)-**3c** unless otherwise noted (see the supplementary material). [g] c 5.0–5.1 in CHCl$_3$ unless otherwise noted. [h] **1**/**2**/RhH(CO)(PPh$_3$)$_3$/TRAP = 1000/1500/1/1.1. [i] Neat **2** was added within 1 min. [j] Isolated yield by MPLC. [k] Determined by HPLC analysis of N-(3,5-dinitrophenyl) amide derivatives with chiral stationary phase column Sumichiral OA-4400 (4 mm × 25 cm). [l] Determined by X-ray crystal structure of an amide derivative with (S)-[1-(1-naphthyl)ethyl]amine (see the supplementary material). [m] c 5.08 in EtOH.

Excellent catalyst turnover efficiency for the reaction with acrolein is shown in entry 12, where the [substrate]/[catalyst] ratio was raised to 1000/1 without significant loss of the enantiomeric purity of product.

A gram-scale experimental procedure is given for the reaction of **1c** with acrolein (**2g**) (entry 12); a mixture of RhH(CO)(PPh$_3$)$_3$ (9.2 mg, 0.010 mmol), (S,S)-(R,R)-TRAP (8.8 mg, 0.011 mmol), and **1c** (1.38 g, 9.80 mmol) in benzene (30 mL) was stirred at room temperature for a few minutes and then cooled to 3 °C. To the well-stirred slurry mixture was added a solution of **2g** (0.86 g, 15.3 mmol) in benzene (20 mL) over a period of 6 h at 3 °C, and the resulting mixture was stirred for 1 h. After the catalyst was removed by passing the solution through a short column of silica gel (3 × 3 cm, hexane/ethyl acetate = 1/1), bulb-to-bulb distillation gave 1.73 g (89%) of (R)-**9**, whose enantiomeric excess was determined to be 84% by GLC analysis with chiral capillary column Chiraldex G-TA (0.25 mm × 30 m, base line separation).

The Michael addition of **1b** with **2a** employing conventional cis-chelating chiral diphosphines such as BINAP, DIOP, or CHIRAPHOS was much less enantioselective (<17% ee),[10] suggesting that the trans-chelation of chiral ligand to rhodium is crucial for the highly stereoselective Michael addition, even if the possibility of other coordination modes of TRAP in catalytically active species cannot be excluded at this stage.[11] The X-ray crystal structure analysis[12] of *mer*-RuH(NCCHCO$_2$Me)(NCCH$_2$CO$_2$Me)(PPh$_3$)$_3$, formed by the oxidative addition of methyl cyanoacetate onto Ru(C$_2$H$_4$)(PPh$_3$)$_3$, reveals that the activated cyanoacetate (NCCHCO$_2$Me group), which bonds to the ruthenium not through the methine carbon but through the cyano nitrogen, undergoes the Michael addition.[12] It may be conceived that the present rhodium-catalyzed Michael addition involves the similar enolate intermediate in which the enantioselective carbon–carbon bond formation would be accomplished at the carbon atom very distant from the metal center as shown in Scheme II. The remote enantiofacial differentiation may be achieved effectively by the concave chiral surroundings of TRAP rather than the convex chiral surroundings of cis-chelating diphosphine ligands.

Mechanistic studies and further synthetic applications of TRAP are now in progress in our laboratory.

Acknowledgment. We thank Mr. Yoshiki Nakagawa for technical assistance on the X-ray studies, Prof. Sanshiro Komiya (Tokyo University of Agriculture and Technology) for kindly providing us with the crystal coordinates for the ruthenium complex, and Prof. Günter Helmchen (University of Heidelberg) for valuable discussions.

Supplementary Material Available: Listings of ^{1}H and ^{13}C NMR, IR, and analytical data for the Michael adducts **3–9**, details of the experimental procedure for the determination of the absolute configurations of **3–9**, and tables of data from the X-ray studies of the (S)-N-[1-(1-naphthyl)ethyl] amide derivative (10 pages). Ordering information is given on any current masthead page.

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(10) The enantiomeric excesses in the reactions at 5 °C with the cis-chelating ligands were as follows: BINAP, 17% ee; DIOP, 12% ee; CHIRAPHOS, 3% ee.

(11) The ^{31}P NMR (toluene-d_8) spectrum of an equimolar mixture of RhH(CO)(PPh$_3$)$_3$ and TRAP (1.7×10^{-2} M) showed the existence of several undefined Rh–TRAP species at a temperature range from −60 to 0 °C.

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Hydride and Halide Ligand Effects on the Enthalpies of Protonation of Transition Metal Complexes

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In previous studies from this laboratory, the basicities of metals in transition metal complexes have been determined calorimetrically by measuring their enthalpies of protonation with CF$_3$SO$_3$H in 1,2-dichloroethane solvent. Using this method, the effects of different methyl-substituted cyclopentadienyl ligands in (η^5-C$_5$Me$_x$H$_{5-x}$)Ir(1,5-cyclooctadiene),[1] monodentate phosphines in (η^5-C$_5$H$_5$)Ir(CO)(PR$_3$) and Fe(CO)$_3$(PR$_3$)$_2$,[2] and the chelating phosphines in Fe(CO)$_3$($\widehat{P\ P}$),[3a] M(CO)$_2$($\widehat{P\ P}$)$_2$ (M = Cr, Mo, W),[3b] and W(CO)$_3$(tridentate phosphine)[4] have been investigated. In the present communication we compare the different effects of halide and hydride ligands on the basicity of the metal in

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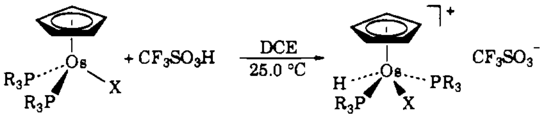
Table I. Enthalpies of Protonation (ΔH_{HM}) and ^{1}H NMR Data for $CpOs(PR_3)_2X$ and $CpOs(PR_3)_2(X)(H)^+$ Complexes

compound	$-\Delta H_{HM}$,[a] kcal/mol	^{1}H NMR:[b,c] Cp
$CpOs(PPh_3)_2Cl$ (**1**)	19.7 (±0.2)	4.30 (s)
1H$^+$		5.43 (s)
$CpOs(PPh_3)_2Br$ (**2**)	16.3 (±0.1)	4.31 (s)
2H$^+$		5.43 (s)
$CpOs(PPh_3)_2I$ (**3**)	14.1 (±0.1)	4.34 (s)
3H$^+$		5.35 (s)
$CpOs(PPh_3)_2H$ (**4**)	37.3 (±0.1)	4.28 (s)
4H$^+$		4.98 (s)
$CpOs(PPh_2Me)_2Br$ (**5**)	20.0 (±0.2)	4.50 (s)
5H$^+$		5.66 (s)
$CpOs(PPh_2Me)_2H$ (**6**)	39.2 (±0.3)	4.30 (s)
6H$^+$		5.14 (s)

[a] For protonation with CF_3SO_3H (0.1 M) in DCE solvent at 25.0 °C. Errors are given as the average deviations from the mean of at least four titrations. [b] Chemical shifts in ppm in CD_2Cl_2 with TMS (δ = 0.00 ppm) at room temperature. [c] δ and $^2J_{PH}$ values for the hydride ligands are as follows: **1H$^+$**, −11.66 (t, 32.4 Hz); **2H$^+$**, −12.13 (t, 34.0 Hz); **3H$^+$**, −12.74 (t, 34.7 Hz); **4**, −14.56 (t, 27.9 Hz); **4H$^+$**, −11.53 (t, 29.0 Hz); **5H$^+$**, −12.70 (t, 33.4 Hz); **6**, −15.23 (t, 28.4 Hz); **6H$^+$**, −12.57 (t, 30.6 Hz).

$CpOs(PR_3)_2X$ complexes, where Cp = η^5-C_5H_5, PR_3 = PPh_3 or PPh_2Me, and X = Cl, Br, I, or H. In all of these complexes, the metal is formally in the +2 oxidation state; yet it is found that the osmium is up to 23.2 kcal/mol more basic in the hydride than in the analogous halide complexes.

Of the complexes studied, $CpOs(PPh_3)_2Cl$ (**1**),[5] $CpOs(PPh_3)_2Br$ (**2**),[6] $CpOs(PPh_3)_2I$ (**3**),[5] and $CpOs(PPh_3)_2H$ (**4**)[7] have been reported previously; **2** and **4** are known[5] to be protonated by strong acids. Compounds $CpOs(PPh_2Me)_2Br$ (**5**)[8] and $CpOs(PPh_2Me)_2H$ (**6**)[7] were prepared by analogy with literature methods and characterized by elemental analysis and ^{31}P and ^{1}H NMR spectra. All the compounds **1–6** are protonated rapidly and quantitatively at the metal centers with 1 equiv of CF_3SO_3H, as evidenced by the hydride signals in the ^{1}H NMR spectra (Table I). The trans structure of the $CpOs(PR_3)_2(X)(H)^+$ (X = halide) products is established by the triplet hydride resonance. The structures of $CpOs(PR_3)_2(H)_2^+$, **4H$^+$** and **6H$^+$**, are also proposed to be trans on the basis of studies by Chinn and Heinekey,[9] who observed two distinct ^{1}H NMR hydride ($^2J_{PH}$ = 29.4–30.7 Hz) signals for $CpRu[(R)\text{-}(+)\text{-}Ph_2PCH_2CH(CH_3)PPh_2](H)_2^+$; this rules out the cis isomer. They assigned trans structures to the analogous $CpRu(PR_3)_2(H)_2^+$ compounds because they have similar coupling constants ($^2J_{PH}$ = 23.3–30.7 Hz). Complexes **4H$^+$** and **6H$^+$** are also assigned trans structures on the basis of their $^2J_{PH}$ values of 29.0 and 30.6 Hz, respectively.



(1)

1-6 **1H$^+$-6H$^+$**

Calorimetric titration of complexes **1–5** with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) solution at 25.0 °C as previously described[1,10] has yielded their enthalpies of protonation (ΔH_{HM}, eq 1).[11] Because of small amounts of decomposition in the calorimeter, the ΔH_{HM} of **6** was determined from equilibrium constant (K_{eq}) measurements (eq 2) at different temperatures.

$$\underset{\mathbf{4H^+}}{[trans\text{-}CpOs(PPh_3)_2(H)_2^+]} + \underset{\mathbf{6}}{CpOs(PPh_2Me)_2H} \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{4}}{CpOs(PPh_3)_2H} + \underset{\mathbf{6H^+}}{[trans\text{-}CpOs(PPh_2Me)_2(H)_2^+]} \quad (2)$$

This study was performed using 0.02 mmol of $[trans\text{-}CpOs(PPh_3)_2(H)_2^+][CF_3SO_3^-]$ (**4H$^+$**) and 0.02 mmol of **6** in 0.5 mL of CD_2Cl_2 in an argon-filled air-tight NMR tube. After the sample was allowed to equilibrate for at least 8 h, during which time equilibrium was established, the intensities of the Cp resonances were measured; the concentrations of the species in solution, K_{eq}, ΔH_{HM}, $\Delta\Delta S$, and $\Delta\Delta G$ were then calculated.[12]

The ΔH_{HM} values in Table I show that the basicities of the hydride compounds **4** and **6** (ΔH_{HM} = −37.3 and −39.2 kcal/mol, respectively) are much higher than those of the analogous bromo compounds **2** and **5** (ΔH_{HM} = −16.3 and −20.0 kcal/mol, respectively).[13] The magnitude of these differences is illustrated by estimated ratios of equilibrium constants (K) for the bromide–hydride pairs of complexes. Since $\Delta\Delta S$ for reaction 2 is only −1.0 (±1.0) eu, the value of $T\Delta\Delta S$ = −0.30 kcal/mol is small compared to $\Delta\Delta H$ (−1.9 ± 0.3 kcal/mol); thus, $\Delta\Delta G \sim \Delta\Delta H$ and $\Delta\Delta H \sim -RT \ln K$. Assuming that $\Delta\Delta S$ is also small for the equilibrium constant comparisons of **2** vs **4** and **5** vs **6**, $CpOs(PPh_3)_2H$ is 2.5 × 10^{15} times (i.e., $\Delta\Delta H$ = 21.0 kcal/mol) more basic than $CpOs(PPh_3)_2Br$, and $CpOs(PPh_2Me)_2H$ is 1.2 × 10^{14} times (i.e., 19.2 kcal/mol) more basic than $CpOs(PPh_2Me)_2Br$. While these comparisons are approximate, they do show that the hydride complexes **4** and **6** are dramatically more basic than the bromide and other halide analogs of $CpOs(PR_3)_2X$ (Table I).

The basicity of the metal in compounds $CpOs(PPh_3)_2X$ (**1–3**) changes relatively little with changes in the halide but increases in the order $I^- < Br^- < Cl^-$. One might have expected the reverse order[14] since the higher electronegativity and lower polarizability of Cl^- should decrease the electron density on the metal. On the other hand, the electron-donor abilities of the halides increase in the order $I^- < Br^- < Cl^-$. This may be seen in the gas-phase proton affinities (PA):[15] I^- (314.3 kcal/mol) < Br^- (323.6 kcal/mol) < Cl^- (333.3 kcal/mol). The high PA (400.4 kcal/mol) of hydride (H^-) indicates that it should be a much stronger electron donor (i.e., base) than the halides. As the strongest X donor to the Os in the $CpOs(PPh_3)_2X$ complexes, the hydride ligand should make **4** the most basic complex in this series, as is observed (Table I). In fact, there is an excellent correlation (r = 0.9995 for eq 3) between the donor ability of the halide or hydride ligand as measured by the PA of X^-(g) and ΔH_{HM} for complexes **1–4**. The

$$-\Delta H_{HM} = 0.2698(PA) - 70.64 \quad \text{(in kcal/mol)} \quad (3)$$

idea that strong donor ligands enhance the basicities of their metal complexes has been quantitated in correlations between phosphine basicities (ΔH_{HP}) and metal basicities (ΔH_{HM}) in $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$.[2] Equation 3 is another type of ligand basicity vs complex basicity correlation, but one that uses PA as a measure

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(11) Plots of temperature vs amount of acid were linear. There was no decomposition of either the neutral or the protonated species during the titration, as evidenced by the normal pre- and posttitration base-line slopes for **1–5**.

(12) The measured K_{eq} values at various temperatures: 15.0 °C, 15.4; 20.0 °C, 15.3; 22.5 °C, 15.1; 25.0 °C, 14.6; 27.5 °C, 14.2; 30.0 °C, 13.2; 35.0 °C, 12.7. $\Delta\Delta G = -RT \ln K_{eq}$ = −1.6 kcal/mol at 25.0 °C. ΔH_{HM} was calculated from a plot of $\ln K_{eq}$ vs $1/T$ where the slope = $-\Delta\Delta H/R$. $\Delta\Delta S$ was calculated from $\Delta\Delta H_{HM} = \Delta\Delta G + T\Delta\Delta S$ with $\Delta\Delta H_{HM}$ = −1.9 (±0.3) kcal/mol.

(13) Although solvation effects can be substantial (see, for example: Sharpe, P.; Richardson, D. E. *J. Am. Chem. Soc.* **1991**, *113*, 8339–8346), the similarities in structures of the reactants and the products here suggest that solvation does not affect the observed trends in ΔH_{HM}.

(14) This reverse trend was observed for reactions of HCl and CF_3SO_3H with the 16-electron square planar complexes $Ir(X)(CO)(PR_3)_2$, but these data also reflect the coordination of a sixth ligand. Pearson, R. G.; Kresge, C. T. *Inorg. Chem.* **1981**, *20*, 1878–1882.

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of ligand basicity. Since PA values are known[15] for a variety of anions (A^-) (e.g., F^-, CN^-, $CH_3CO_2^-$, $C{\equiv}CH^-$, and CH_3^-), eq 3 allows one to estimate basicities of a range of $CpOs(PPh_3)_2(A)$ complexes. Perhaps in other complexes, one might also find that the basicity of the metal increases as the PA values of its A^- ligands increase.

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Periodic Polymerization of Acrylonitrile in the Cerium-Catalyzed Belousov–Zhabotinskii Reaction

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We have studied the effects of acrylonitrile on the cerium-catalyzed Belousov–Zhabotinskii (BZ) reaction and have found that they depend on when the monomer is added to the batch reaction. Moreover, we have found that the polymerization of acrylonitrile occurs periodically. We believe this to be the first report of an isothermal, periodic polymerization.

The study of polymerization reactions as dynamical systems is relatively rare although the potential utility is great. Ray and co-workers have investigated oscillatory thermal phenomena in a continuous-flow stirred-tank reactor (CSTR) for vinyl polymerizations.[1-3] Propagating fronts of addition polymerization have been studied in the former Soviet Union[4-8] and in the U.S.[9-11]

Vãradi and Beck observed that acrylonitrile could inhibit oscillations in the ferroin-catalyzed BZ reaction and a white precipitate would form.[12] Because ferroin can complex with the polymer, we have chosen the cerium–catalyzed system instead.

Acrylonitrile (Aldrich) was obtained with MEHQ inhibitor. The presence of the inhibitor was found to not alter the results. All other chemicals were of reagent grade (Aldrich) and used without further purification. Reactions were performed in a beaker open to the air at ambient conditions (23 °C) with magnetic stirring. The BZ reaction was prepared[13] from 10 mL of each of the following stock solutions: 0.23 M sodium bromate ($NaBrO_3$), 0.31 M malonic acid ($CH_2(COOH)_2$), and 0.019 M ammonium cerium(IV) nitrate ($Ce(NH_4)_2(NO_3)_6$) in 2.7 M H_2SO_4.

The malonic acid and bromate solutions were mixed. The cerium solution was then added, and the data acquisition was begun. The signals from the bromide-selective electrode (Orion) and the platinum electrode (Rainin) (both referenced to a Hg/$HgSO_4$ electrode (Rainin)) were digitized on a Strawberry Tree 12 bit A/D board and collected on a Macintosh IIcx computer.

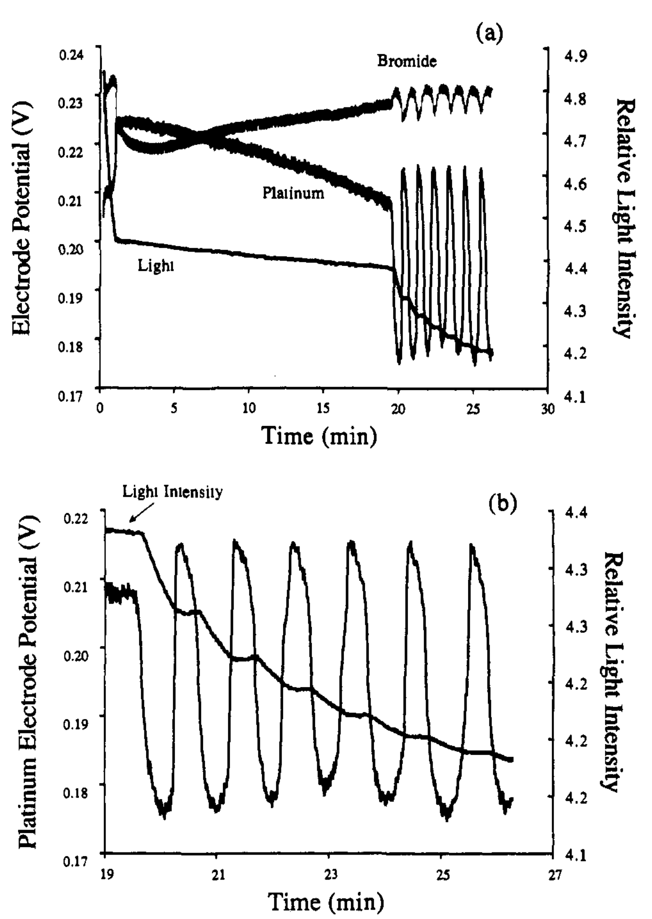

Figure 1. (a) Evolution of a BZ reaction in which 1.0 mL of acrylonitrile was present before addition of Ce(IV)/H_2SO_4 solution: total volume = 30.0 mL; $[NaBrO_3]_0$ = 0.077 M; [malonic acid]$_0$ = 0.10 M; [Ce(IV)] = 0.0063 M; $[H_2SO_4]_0$ = 0.90 M. (b) Enlargement of the oscillatory region.

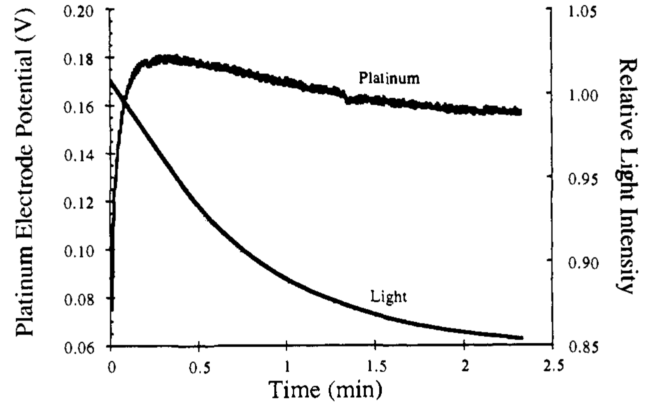

Figure 2. Acrylonitrile polymerization initiated by Ce(IV) and malonic acid. The acrylontrile (1.0 mL) and malonic acid were stirred before the Ce(IV)/H_2SO_4 solution was added. Reagents: [malonic acid]$_0$ = 0.10 M; [Ce(IV)] = 0.0063 M; $[H_2SO_4]_0$ = 0.90 M.

Because polyacrylonitrile is insoluble in water, the qualitative progress of the polymerization was monitored by measuring the relative decrease in transmitted light due to scattering of an incandescent light beam passed through the solution. A simple CdS detector was used without calibration by converting the current to a voltage and using that voltage as a measure of the relative intensity.

Figure 1 shows that the oscillations do not commence for 20 min, although the normal induction period for the reaction with these concentrations is 2.8 min. The system remains in the oxidized, low-bromide state. If the acrylonitrile is added before the cerium, polymer forms when the cerium solution is added, but

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