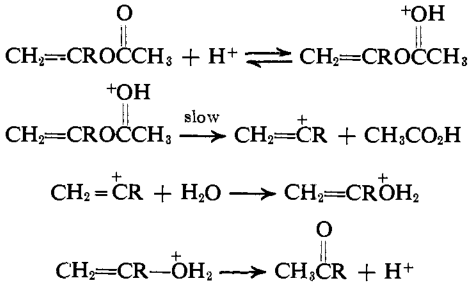
with the fact that there is very little difference in the rates of these compounds at this concentration of acid.

The isotope effect of 2.50 which is observed for compound **1** is similar to the value of 3.25 for compound **6** at higher acidities indicating an ASE2 mechanism. However, if we assume that the rate of compound **6** at $H_0 = 0$ in D_2SO_4 represents the rate at which all of the compounds react in this acidity by the normal ester mechanism, then we can calculate the isotope effect due just to the ASE2 mechanism for compound **1**. This assumption seems quite warranted by the fact that at $H_0 = 0$ compounds **3–6** all react at virtually the same rate in H_2SO_4 and that they all have similar isotope effects. Furthermore, a deuterated medium will favor the normal mechanism even more. It is also necessary to assume an isotope effect of 0.75 for this mechanism which also seems borne out by Table IV. Using these values the isotope effect due solely to the ASE2 mechanism for compound **1** is 3.10. A similar calculation for compound **2** gives a value of 2.42.

Compound **2** is an interesting case at $H_0 = 0$. Using the rate for compound **6** as an approximation to the normal ester rate it can be shown that in D_2SO_4 the rate is 67% due to the normal ester mechanism, and only 33% due to the ASE2 mechanism. However, in H_2SO_4 the predominant mechanism is ASE2 (62% of the rate). Here is a situation where the predominant mechanism depends on whether the solvent is H_2O or D_2O.

There is one more mechanism (eq 9–12) which is a formal possibility and must be eliminated. This involves a protonation of the ester oxygen and then cleavage to the corresponding vinyl cation. As this mechanism does not involve water in the rate-determining step it would be expected to have an acidity dependence similar to the ASE2 mechanism. It would also have a rather sharp dependence on substituent. However, the isotope effect would have to be inverse since it involves a preequilibrium protonation. There is no portion of the acidity range in which all of these requirements are simultaneously satisfied for any of the compounds studied.



$$\mathrm{CH_2{=}CRO\overset{\overset{O}{\|}}{C}CH_3 + H^+ \rightleftharpoons CH_2{=}CRO\overset{\overset{^{+}OH}{\|}}{C}CH_3} \tag{9}$$

$$\mathrm{CH_2{=}CRO\overset{\overset{^{+}OH}{\|}}{C}CH_3 \xrightarrow{slow} CH_2{=}\overset{+}{C}R + CH_3CO_2H} \tag{10}$$

$$\mathrm{CH_2{=}\overset{+}{C}R + H_2O \longrightarrow CH_2{=}CR\overset{+}{O}H_2} \tag{11}$$

$$\mathrm{CH_2{=}CR{-}\overset{+}{O}H_2 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}R + H^+} \tag{12}$$

Another way of eliminating this possibility is by examination of the relative stabilities of the α-phenyl vinyl cation and the benzyl cation. The SN1 rate of solvolysis of $PhCBr{=}CH_2$ in 80% EtOH at 170° is 6.0×10^{-6} sec^{-1},[27] whereas the SN1 rate of solvolysis of $PhCH_2Br$ in 90% EtOH at 30° may be calculated to be approximately 1.2×10^{-6}.[28]

Thus, it can be readily seen that $PhCH_2^+$ is a much more stable entity than $PhC^+H{=}CH_2$. However, the hydrolysis of benzyl acetate by cleavage to the benzyl cation does not become significant until about 65% sulfuric acid. At 65% H_2SO_4 the rate is 1.7×10^{-3} sec^{-1}.[16]

Therefore, the rate of α-acetoxystyrenes by this mechanism would be even slower by several orders of magnitude. As the rate of α-acetoxystyrene extrapolated to 65% H_2SO_4 is about 6.3 sec^{-1}, this mechanism is completely excluded.

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[27] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).

[28] The calculation was performed by assuming a ρ of -5 and using the rate for p-$CH_3OC_6H_4CH_2Cl$ (J. W. Baker, *J. Chem. Soc.*, 2506 (1951)) along with the fact that alkyl bromides react about 40 times faster than alkyl chlorides (A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 82).

Kinetics of the Cerium (IV) Oxidation of Benzaldehyde[1]

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Contribution from the Department of Chemistry, Yale University,
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Abstract: The kinetics of the cerium(IV) oxidation of benzaldehyde to benzoic acid were studied in 85% aqueous acetic acid. The first reaction was the formation of a 1:1 benzaldehyde–ceric ion complex. This was followed by an acid-catalyzed decomposition of the complex as well as of a 2:1 benzaldehyde-ceric ion complex which is present in relatively low concentration. Evidence was found for the formation of benzoyl radicals as an intermediate, and the reaction was found to give a kinetic isotope effect.

Cerium(IV) is one of a group of metal ion oxidants which apparently react only *via* one-electron steps. Thus, in the oxidation of thallium(I) by ceric nitrate,[3] kinetic results indicate the intermediacy of the highly unstable thallium(II) species rather than a two-electron step leading to cerium(II). The oxidation of chromium(III) to chromium(VI) by ceric sulfate also was shown to proceed *via* consecutive one-electron steps.[4]

A typical mode of oxidation of aliphatic aldehydes and ketones by one-electron metal ion oxidants involves coordination with the carbonyl group followed by the

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[1] This investigation was supported by the National Science Foundation.

[2] Taken in part from the Ph.D. Thesis of P. C. F., 1966. National Institutes of Health Predoctoral Fellow, 1963–1966.

[3] M. C. Dorfman and J. W. Gryder, *Inorg. Chem.*, **1**, 799 (1962).

[4] J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).

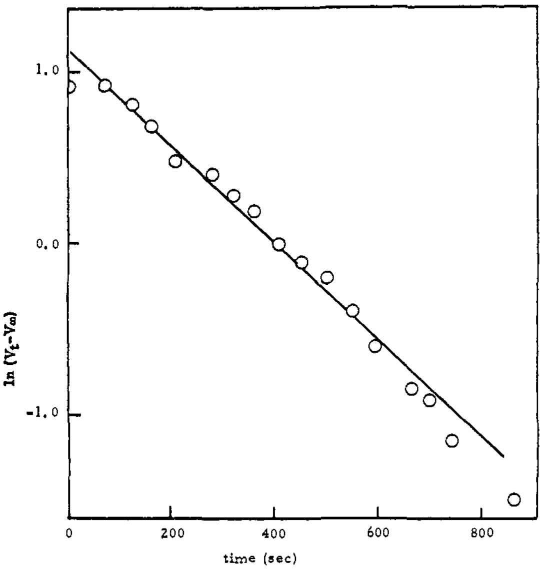
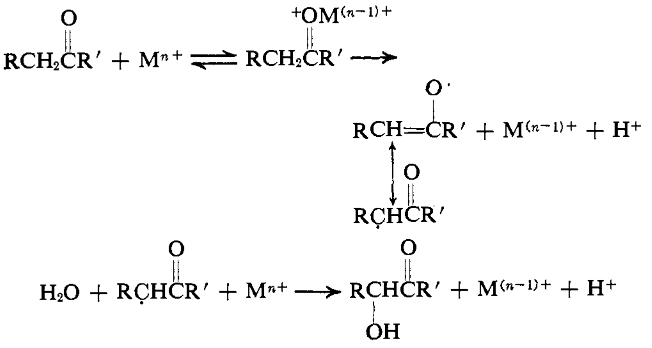


Figure 1. Titrimetric run at 0.3 M $HClO_4$.

loss of an α-hydrogen. The organic intermediate reacts with a second equivalent of the oxidant to give an acetol, a ketol, or related compound.



$$RCH_2\overset{O}{\overset{\|}{C}}R' + M^{n+} \rightleftharpoons RCH_2\overset{{}^{+}OM^{(n-1)+}}{\overset{\|}{C}}R' \longrightarrow RCH{=}\overset{O\cdot}{\overset{|}{C}}R' + M^{(n-1)+} + H^+ \updownarrow R\dot{C}H\overset{O}{\overset{\|}{C}}R'$$

$$H_2O + R\dot{C}H\overset{O}{\overset{\|}{C}}R' + M^{n+} \longrightarrow R\underset{\underset{OH}{|}}{C}H\overset{O}{\overset{\|}{C}}R' + M^{(n-1)+} + H^+$$

As a result, nonenolizable aldehydes such as benzaldehyde and pivaldehyde are not easily oxidized by many of these reagents.

Cerium(IV) was of interest to us since it is readily reduced by benzaldehyde. Thus, we have carried out an investigation of the reaction in aqueous acetic acid solution. The stoichiometry of the reaction was first determined by allowing 0.23 M ceric perchlorate in 47% acetic acid to react with an excess of benzaldehyde. Except for a very small amount of a brownish substance, the only organic products were benzoic acid and unreacted benzaldehyde. Based on the expected 2:1 stoichiometry, the yield of isolated benzoic acid was 89%. The possibility that some benzil might be formed as a product was checked by an isotope dilution experiment using benzaldehyde-7-^{14}C as the substrate. The maximum yield of benzil was found to be 0.01%.

The kinetic studies were carried out in 85% aqueous acetic acid and the rate of disappearance of cerium(IV) was determined both spectrometrically and titrimetrically. The aldehyde and ceric solutions were thoroughly degassed before mixing since oxygen was found to have a marked effect on the rate of reaction. Ceric perchlorate was used as the oxidant and perchloric acid was used as the catalyst since the perchlorate ion appears not to form stable complexes with cerium(IV).

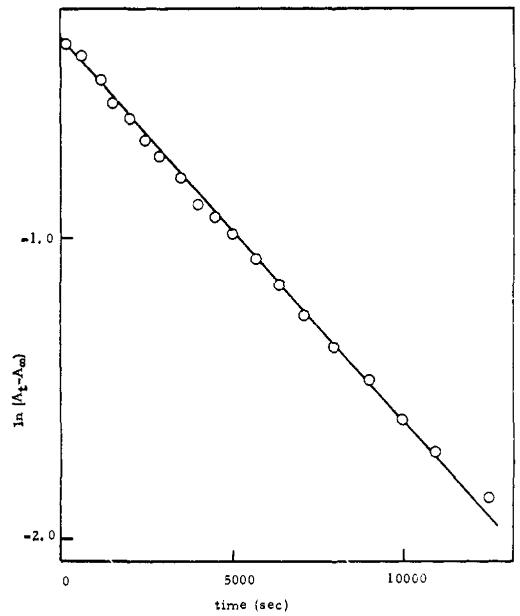


Figure 2. Spectrometric kinetic run at 0.05 M $HClO_4$.

Nitrate ion, which does form complexes with cerium(IV),[5] was found to markedly retard the reaction.

The results from a typical titrimetric run carried out in the presence of excess benzaldehyde and perchloric acid are shown in Figure 1. The linearity of the rate plot indicates the reaction to be first order in oxidant. This characteristic of the kinetic data proved to be consistent over a 12-fold range in perchloric acid concentration which gave a 60-fold range in the pseudo-first-order rate constant, k_{ox}.

The results from typical spectrophotometric runs carried out at different perchloric acid concentrations are shown in Figures 2–4. At the lower acid concentrations, 0.1 M or less, the first-order plots are quite good (ignoring for the moment the initial rapid decrease in absorbance), and the slopes of the plots are equivalent to the titrimetric rate constants. In contrast, at higher acid concentrations, the curvature of the plots is very severe and the slopes of the level portion of the curves are wavelength dependent and less than the titrimetric rate constants (Table I). At lower wavelengths, the spectrophotometric rate constant approaches the titrimetric value; however, below 380 mμ interference by the benzaldehyde spectrum prevented determination of reaction rates.

Table I. Effect of Wavelength on the Measured Rate Constants for Spectrometric Runs with 0.3 M Perchloric Acid[a]

Run	Wavelength, mμ	$k_{ox} \times 10^3$, sec^{-1}
Spectrometric	380	2.51 ± 0.01
	400	1.52
	420	0.81 ± 0.02
Titrimetric		2.95 ± 0.13

[a] Concentrations: Ce(IV) = 0.005 M, RCHO = 0.025 M, 85% aqueous HOAc, 25°, ionic strength = 0.6.

Several complications of the reaction system tended to give less than ideal reproducibility. Oxygen strongly

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(5) *Cf.* K. B. Wiberg and P. C. Ford, *Inorg. Chem.*, 7, 369 (1968).

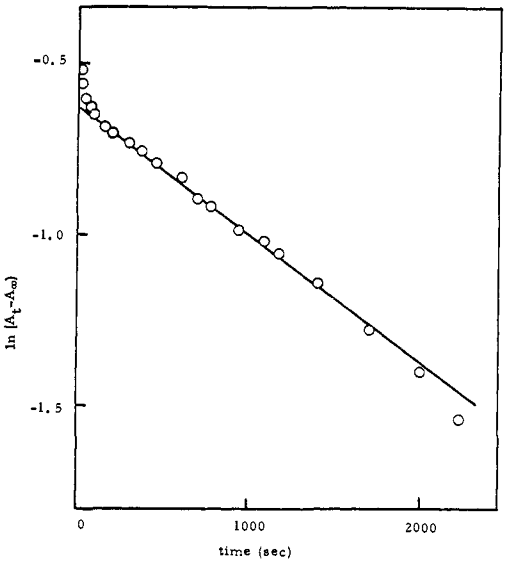

Figure 3. Spectrophotometric kinetic run at 0.1 *M* $HClO_4$.

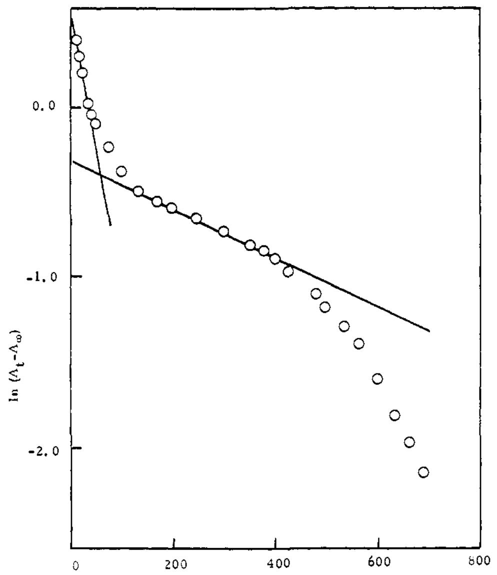

Figure 4. Spectrometric kinetic run at 0.3 *M* $HClO_4$.

accelerated the reaction and as a consequence very careful degassing was required. In a typical experiment the pseudo-first-order constant decreased from 93 × 10^{-3} sec^{-1} in the presence of oxygen to 1.14 × 10^{-3} sec^{-1} after two degassing cycles, and to 0.55 sec^{-1} after four cycles. Cerium(IV) solution had only limited stability in aqueous acetic acid, and as a result, these had to be made up on the same day the kinetic experiments were performed. The reproducibility is indicated by the data in Table II which correspond to a single set of concentrations.

Table II. Reproducibility of Kinetic Runs[a]

Run	Series	$k_{ox} \times 10^3$, sec^{-1}
Spectrometric	I	0.100
	I	0.174
	I	0.122
	II	0.129
	II	0.129
	II	0.122
	II	0.118
	II	0.123
	II	0.109
Titrimetric	III	0.195
	IV	0.138
	IV	0.117
Av		0.131 ± 0.19
Av (excluding entries 2 and 10)		0.121 ± 0.07

[a] [Ce(IV)] = 0.0052 *M*; [$HClO_4$] = 0.05 *M*; [C_6H_5CHO] = 0.025 *M*, μ = 0.60; 85% aqueous HOAc, 25°.

The initial rapid decrease in absorbance apparent in Figures 3 and 4 was observed in all kinetic runs where the acid concentration exceeded 0.07 *M*. Evidence that this rapid absorbance change does not represent an oxidation comes from a comparison of titrimetric runs with spectrometric runs at the same acid concentration (Figures 1 and 4). A spectrometric run under the same conditions in the absence of benzaldehyde gave no comparable decrease in absorbance but rather gave a small increase due to the dissociation of the polymeric ceric species to correct for the dilution effect.[5]

Since the initial absorbance change does not involve oxidation, but does involve both cerium(IV) and benzaldehyde, it appears probable that a complex is formed between the two reactants. The absorbance of the solution after complex formation has occurred, but before significant oxidation has occurred, may be estimated from the intersection of the lines in Figure 4. This value divided by the ceric concentration gives the apparent absorbancy index (ϵ_{eq}) for the equilibrium mixture of complexed and noncomplexed cerium(IV). The magnitude of ϵ_{eq} shows little change over a 12-fold variation in acid concentration (Table III and Figure 5) whereas the initial absorbancy index (ϵ_i) nearly triples.

Table III. Effect of Perchloric Acid Concentration on ϵ_i and ϵ_{eq}[a]

[$HClO_4$], *M*	ϵ_i	ϵ_{eq}
0.0241	138 ± 2	143 ± 3
0.051	159 ± 1	159 ± 1
0.100	177 ± 2	158 ± 6
0.229	261 ± 9	136 ± 10
0.301	343 ± 1	140 ± 4

[a] [Ce(IV)] = 0.0051 *M*; [C_6H_5CHO] = 0.025 *M*; μ = 0.6, 85% HOAc, 25.0°.

These data indicate either that the equilibria constituting complex formation are relatively insensitive to changes in acid concentration or that complex formation is so favored that changes in the equilibrium do not influence ϵ_{eq}. Although changes in acid concentration had little effect on ϵ_{eq}, changes in benzaldehyde concentration has a large effect (Figure 6). These data suggest that complex formation is essentially complete at 0.05 *M* benzaldehyde.

Our previous investigation of ceric ion equilibria in aqueous acetic acid indicated that the principal species are the monomer and trimer, and that the species with a high absorbancy index is the monomer.[5] The increase in ϵ_i with increasing acid concentration results from a shift in the monomer–trimer equilibrium which responds to the cube of the acid concentration. The constant for the above equilibrium and the absorbancy indices are available from this investigation.[5]

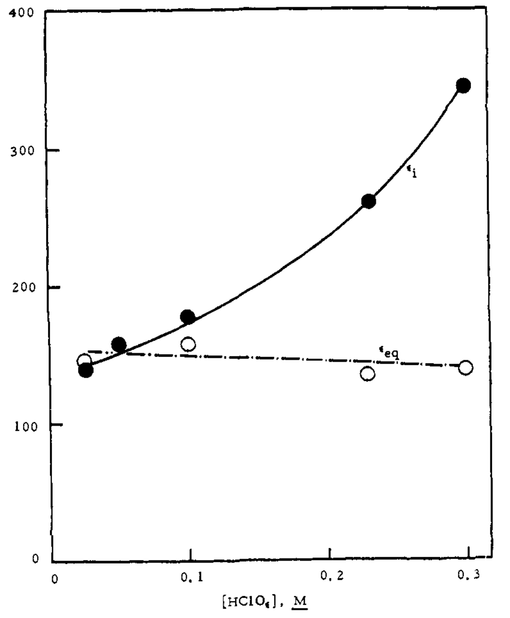

Figure 5. Effect of acid concentration on absorbancy indices (400 mμ).

The equilibrium constant for benzaldehyde complex formation was estimated using the following model.

$$3M \overset{K_1}{\rightleftharpoons} T$$

$$C_6H_5CHO + M \overset{K_2}{\rightleftharpoons} C$$

$$[Ce(IV)]_{tot} = 3[T] + [M] + [C]$$

$$\epsilon_{eq}[Ce(IV)]_{tot} = \epsilon_T[T] + \epsilon_M[M] + \epsilon_C[C]$$

where $[Ce(IV)]_{tot}$ is the total number of equivalents of cerium(IV), T is the trimer, M is the monomer, and C is the complex. Using the definitions of the equilibrium constants, the equations may be rewritten as

$$[Ce(IV)]_{tot} = 3K_1[M]^3 + K_2[M][C_6H_5CHO] + [M]$$

$$\epsilon_{eq}[Ce(IV)]_{tot} = \epsilon_T K_1[M]^3 + \epsilon_C K_2[M][C_6H_5CHO] + \epsilon_M[M]$$

giving

$$0 = [(3 - \epsilon_T)/\epsilon_C]K_1[M]^3 + [(1 - \epsilon_M)/\epsilon_C][M] - [(1 - \epsilon_{eq})/\epsilon_C][Ce(IV)]_{tot}$$

At higher aldehyde concentrations, the cubic term in monomer concentration will be negligible in comparison to the first-order term. Then

$$[M]/[Ce(IV)]_{tot} = [(1 - \epsilon_{eq})/\epsilon_C]/[(1 - \epsilon_M)/\epsilon_C]$$

The value of ϵ_C may be estimated from Figure 6 to be 25 at 420 mμ, and ϵ_M can be calculated from the data in ref 5 as approximately 350. Using the value of ϵ_{eq} found with 0.025 M benzaldehyde, one calculates that 91% of the ceric ion is in the form of the complex.

The initial change in absorbance corresponds to the change of monomeric ceric species to the complex having a lower absorbancy index. It seems reasonable to assume that the complex is formed by the reaction of the monomer with the aldehyde. If this is correct, the rate constant for the complex formation may be estimated. The model used is

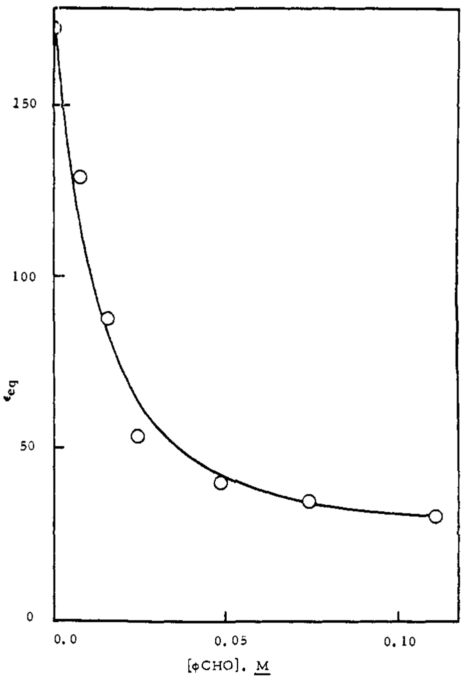

Figure 6. Effect of benzaldehyde concentration on ϵ_{eq} at 420 mμ.

$$T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3M$$

$$M + C_6H_5CHO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{complex (C)}$$

The change in absorbance (A) with time would be given by

$$\frac{dA}{dt} = \epsilon_M\frac{d[M]}{dt} + \epsilon_T\frac{d[T]}{dt} + \epsilon_C\frac{d[C]}{dt}$$

$$= (3\epsilon_M - \epsilon_T)(k_1[T] - k_{-1}[M]^3) + (\epsilon_C - \epsilon_M) \times (k_2[M][C_6H_5CHO] - k_2[C])$$

Since at time zero, $k_1[T] = k_{-1}[M]^3$ and $[C] = 0$, the initial rate would be

$$\left(\frac{dA}{dt}\right)_i = -(\epsilon_M - \epsilon_C)k_2[M][C_6H_5CHO]$$

The initial velocities could be determined by plotting the average rate of absorbance change, $(A_0 - A_t)/t$, against time and extrapolating to zero time. In practice, it was found more convenient to plot the logarithm of this quantity against time giving nearly linear plots (Figure 7) from which the zero time intercept was more easily estimated.

The effect of acid concentration on the initial rates of complex formation was investigated giving the data in Table IV. Since the change in acid concentration also affects the ratio of monomeric to trimeric cerium species, this was taken into account by dividing the initial rates by the monomer concentration calculated from our equilibrium constants.[5] The resultant data are plotted against the acid concentration in Figure 8 and it can be seen that there is a linear relationship. Thus, the rate of complex formation appears to have a first-order dependence on hydrogen ion concentration.

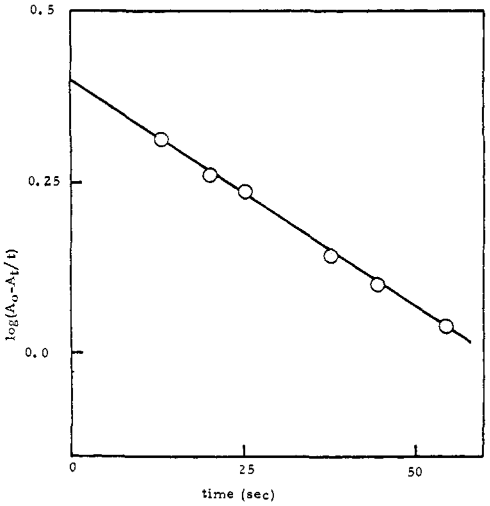

Figure 7. Average rate of decrease in absorbance for complex formation.

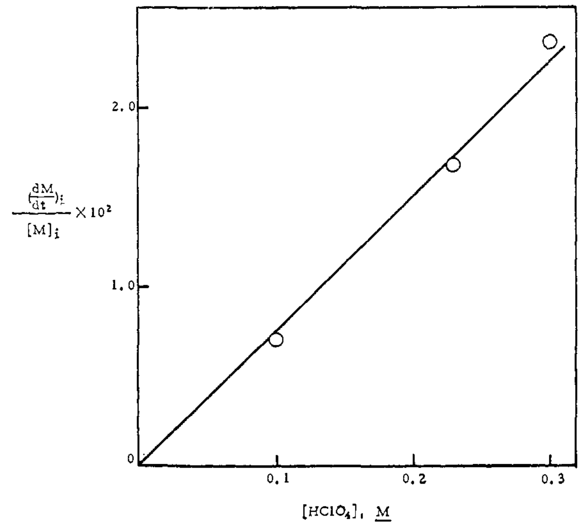

Figure 8. Effect of acid concentration on the initial rate of complex formation.

The effect of benzaldehyde concentration on the rate of complex formation also was investigated giving the data in Table V. Although the initial rates increase with increasing benzaldehyde concentration, they do not rise as rapidly as the aldehyde concentration. This behavior suggests a rate law of the type

$$(d[M]/dt)_i = A[M][RCHO]/(1 + B[RCHO])$$

A plot of the initial rate against 1/[RCHO] should then be linear giving a slope of $1/A[M]$ and an intercept of $B/A[M]$. Figure 9 shows this expectation to be realized.

Table IV. Effect of Perchloric Acid on the Initial Rate of Complex Formation[a]

$[HClO_4]$, M	$[M]_i \times 10^3$, M	$(d[M]/dt)_i \times 10^5$	$(d[M]/dt)_i/[M]_i$
0.10	0.575	0.399	0.00695
0.23	1.24	2.00	0.0161
0.30	1.57	3.64	0.0231

[a] [Ce(IV)] = 0.0050 M, [RCHO] = 0.025 M, μ = 0.6, 85% HOAc, 400 mμ, 25.0°.

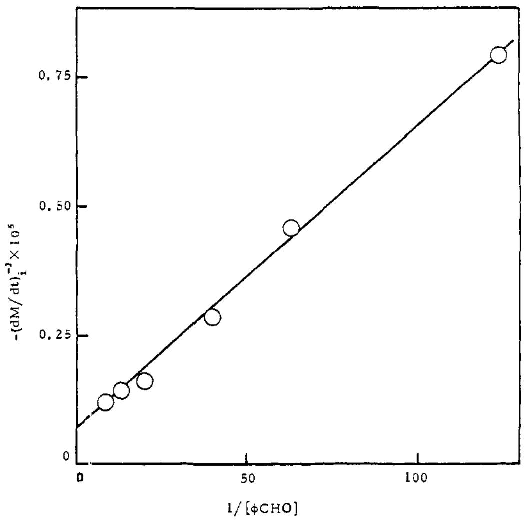

Figure 9. Effect of benzaldehyde concentration on the initial rate of complex formation.

Table V. Effect of Benzaldehyde Concentration on the Initial Rates of Complex Formation[a]

[RCHO], M	$(d[M]/dt)_i \times 10^5$	$(d[M]/dt)_i/[RCHO] \times 10^3$
0.00812	1.26 ± 0.02	1.55
0.0161	2.19 ± 0.13	1.37
0.0247	3.54 ± 0.15	1.43
0.0492	6.30 ± 0.23	1.28
0.0746	6.92 ± 0.41	0.93
0.111	8.20 ± 0.15	0.74

[a] [Ce(IV)] = 0.0050 M, $HClO_4$ = 0.30 M, μ = 0.6, 85% HOAc, 420 mμ, 25°.

A mechanism consistent with this rate law would involve the reaction of benzaldehyde with a ceric monomer which is in a small steady-state concentration and is formed from the predominant form of the ceric monomer by an acid-catalyzed reaction.

$$M + H^+ \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} M'$$

$$M' + RCHO \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} C$$

The initial velocity of complex formation would be

$$(d[C]/dt)_i = k_b[M'][RCHO]$$

Applying the steady-state approximation to M′

$$(d[M']/dt)_i = 0 = k_a[M][H^+] - k_{-a}[M'] - k_b[M'][RCHO]$$

$$[M'] = k_a[M][H^+]/(k_{-a} + k_b[RCHO])$$

then

$$(d[C]/dt)_i = \frac{k_a k_b[M][RCHO][H^+]}{k_{-a} + k_b[RCHO]}$$

The initial rate of disappearance of monomeric cerium(IV) must equal the rate of formation of complex.

Thus, this expression is of the form required by the experimental data, where $A = k_a k_b[H^+]/k_{-a}$ and $B = k_b/k_{-a}$.

The first-order term in acid concentration suggests that M is $CeOR^{3+}$ and M′ is Ce^{4+}

$$CeOR^{3+} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ce^{4+} + HOR$$

where OR^- is either OAc^- or OH^-.[5] By combining this step with complex formation

$$Ce^{4+} + R'CHO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$

the rate law becomes

$$-\left(\frac{d[M]}{dt}\right)_i = \frac{k_1k_2[H^+][R'CHO][M]}{k_{-1}[ROH] + k_2[R'CHO]}$$

The intercept in Figure 9 (4.95×10^3 l. mol^{-1} sec^{-1}) equals $1/k_1[H^+][M]$ giving $k_1 = 0.431$ l. mol^{-1} sec^{-1}. The slope in Figure 9 (6.07×10^2 sec^{-1}) equals $k_{-1}[ROH]/k_1k_2[H^+][M]$. Knowing k_1, the ratio $k_{-1}[ROH]/k_2$ is found to be 0.123 *M*. The product $k_{-1}[ROH]$ may be treated as a single constant, k_{-1}', as long as the solvent composition is not changed.

The values of k_{-1} and k_2 cannot be determined unless one knows the value of k_1/k_{-1}'. This ratio was estimated using the equilibrium constant for the hydrolysis of Ce^{4+} in water[6]

$$Ce^{4+} + H_2O = CeOH^{3+} + H^+$$

and the constant for the equilibrium[5]

$$CeOH^{3+} + HOAc = CeOAc^{3+} + H_2O$$

The former equilibrium constant is 5.2 mol/l. in water, but a correction for the concentration of water in 85% acetic acid (ignoring the probable changes in activity coefficients) gives a value of 0.81 mol/l. in this solvent. The latter equilibrium has a constant of 5.7 in 85% aqueous HOAc. Combination of these two gives

$$0.185 \text{ l./mol} = k_1/k_{-1}' = \frac{[Ce^{4+}]}{[M][H^+]}$$

where $[M] = [CeOH^{3+}] + [CeOAc^{3+}]$. Although this is at best a very rough estimate, it will be useful in a following comparison. Based on this constant $k_{-1}' = 2.32$ sec^{-1} and $k_2 = 18.9$ l. mol^{-1} sec^{-1}.

The slope of the curve in Figure 8 which gives the effect of perchloric acid on the rate was 0.0736 l. mol^{-1} sec^{-1}. This should equal $k_1k_2[RCHO]/(k_{-1}' + k_2[RCHO])$. Using the above values and $[RCHO] = 0.025$ *M*, the slope was calculated to be 0.0729 indicating the internal consistency of the rate constants which were derived.

The kinetics of the oxidation step may now be considered. The titrimetric method unambiguously measures the rate of disappearance of cerium(IV) species. The linearity of $\ln (V_t - V_\infty)$ *vs.* time plots over a wide range of acid concentration (0.025–0.30 *M*) strongly implies that the oxidation is first order in cerium(IV) despite the possible complication from the monomer–trimer equilibrium. This conclusion is consistent with the assumption that the complex is the species involved in the oxidation step. The induction period noted in the titrimetric runs (Figure 1) also is in agreement with this assumption.

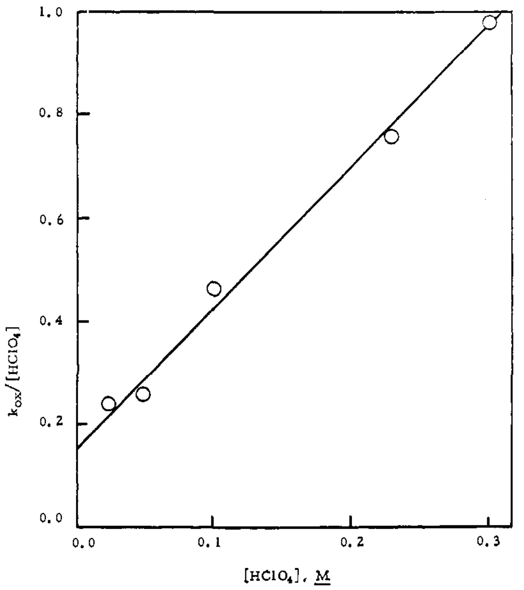

Figure 10. Effect of acid concentration on the titrimetric rate of oxidation, $[C_6H_5CHO] = 0.025$ *M*.

The effect of acid concentration on the titrimetric oxidation rate is recorded in Table VI. It can be seen that there is not a simple first-order dependence. A plot of $k_1/[HClO_4]$ against $[HClO_4]$ (Figure 10) gave a linear relationship indicating both first- and second-order terms

$$v_{ox} = k_1'[H^+][Ce(IV)] + k_2'[H^+]^2[Ce(IV)]$$

where $k_1'[H^+] + k_2'[H^+]^2 = k_{ox}$.

Table VI. Effect of Perchloric Acid Concentration on the Titrimetric Rate Constants[a]

$[HClO_4]$, *M*	$k_{ox} \times 10^3$, sec^{-1}	$k_{ox}/[HClO_4]$
0.024	0.058	0.00241
0.050	0.128 ± 0.010	0.00256
0.101	0.44	0.00435
0.230	1.74 ± 0.03	0.00757
0.301	2.95 ± 0.13	0.00981

[a] $[Ce(IV)] = 0.0051$ *M*, $[RCHO] = 0.025$ *M*, $\mu = 0.60$, 85% HOAc, 25.0°.

The effect of benzaldehyde concentration on the reaction rate is relatively complex. At 0.05 *M* perchloric acid, an increase in benzaldehyde concentration led to a decrease in reaction rate (Table VII). In contrast, changes in concentration had little effect on the rate at 0.1 *M* perchloric acid. Finally, at 0.3 *M* perchloric acid, an increase in benzaldehyde concentration led to an increase in the rate constant.

The data for 0.3 *M* perchloric acid yields a linear plot of $1/k_{ox}$ against $1/[RCHO]$ (Figure 11) suggesting a rate law of the form

$$v = k_{ox}[Ce(IV)] = \frac{A[RCHO][Ce(IV)]}{1 + B[RCHO]}$$

This behavior is typical of a mechanism proceeding *via* partial equilibrium formation of some intermediate species prior to the rate-determining step. However, the preceding evidence indicates that essentially all of the Ce(IV) is in the form of an aldehyde

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(6) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

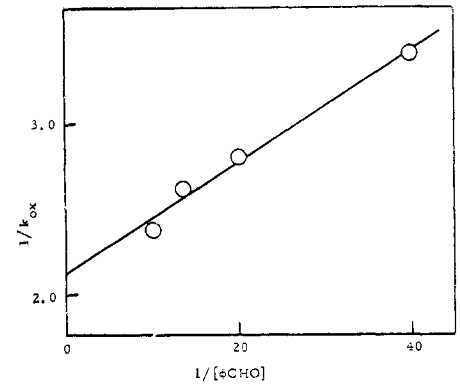

Figure 11. Effect of benzaldehyde on the titrimetric rate of oxidation, $[HClO_4] = 0.3\ M$.

complex. Consequently, the kinetic behavior represented in the above equation cannot be a result of the first benzaldehyde Ce(IV) complex as oxidation proceeding *via* disproportionation of this species would be expected to give zero-order kinetics with respect to aldehyde concentration.

Table VII. Effect of Benzaldehyde Concentration of the Rate of Oxidation[a]

$[H^+]$, *M*	[RCHO], *M*	$k_{ox} \times 10^3$, sec^{-1}	k_{ox}(calcd) $\times$ 10^3, sec^{-1}
0.024	0.025	0.058	0.052
0.05	0.0124	0.151 ± 0.005	0.151
0.05	0.025	0.131 ± 0.019	0.147
0.05	0.052	0.134 ± 0.005	0.142
0.05	0.125	0.099 ± 0.015	0.139
0.05	0.249	0.071 ± 0.008	0.136
0.10	0.025	0.34 ± 0.04	0.42
0.10	0.051	0.36 ± 0.04	0.45
0.10	0.106	0.38 ± 0.01	0.51
0.10	0.438	0.44	0.53
0.23	0.025	1.74	1.79
0.30	0.024	2.95 ± 0.13	2.86
0.30	0.050	3.57	3.56
0.30	0.075	3.83	3.89
0.30	0.100	4.20	4.08

[a] $[Ce(IV)] = 0.0050\ M$, $\mu = 0.6$, 85% HOAc, 25.0°. The rate constants for 0.05 and 0.1 *M* acid are the average for spectrometric and titrimetric runs. At 0.3 *M* perchloric acid, only the titrimetric data are given.

The data then suggest that a second complex is formed having two aldehydes associated with cerium(IV)

$$Ce(IV) + RCHO \overset{K_1}{\rightleftharpoons} C_1$$

$$C_1 + RCHO \overset{K_2}{\rightleftharpoons} C_2$$

where $K_1 \gg K_2$.

The oxidation rate has both a first-order term and a second-order term in acid concentration. This fact, combined with the different effects of changing substrate concentration on the reaction velocity at different acid concentrations may reflect a rate law such as

$$v = k_a[H^+][C_1] + k_b[H^+]^2[C_2]$$

An appropriate rate law may be derived as follows

$$[Ce(IV)]_{total} = [C_1] + [C_2]$$

$$K_2 = \frac{[C_2]}{[C_1][RCHO]}$$

$$[Ce(IV)] = [C_1] + K_2[C_1][RCHO]$$

$$C_1 = \frac{[Ce(IV)]}{1 + K_2[RCHO]}$$

$$C_2 = \frac{K_2[Ce(IV)][RCHO]}{1 + K_2[RCHO]}$$

$$v = \frac{k_1[H^+][Ce(IV)] + k_2K_2[H^+]^2[RCHO][Ce(IV)]}{1 + K_2[RCHO]}$$

At a sufficiently low acid concentration, $k_1[H^+] > k_2K_2[H^+]^2[RCHO]$, and increasing benzaldehyde concentration will depress the rate because of the aldehyde term in the denominator. At higher acid concentrations, $k_2K_2[RCHO][H^+]^2 > k_1[H^+]$ and the second term in the rate law will dominate the kinetic behavior. The relative contributions of the two pathways may be estimated from the results of Figure 10. The intercept corresponds to $k_1/(1 + K_2[RCHO])$ and equals 0.15×10^{-2} l. mol^{-1} sec^{-1} and the slope corresponds to $k_2K_2[RCHO]/(1 + K_2[RCHO])$ and equals 2.70×10^{-2} $l.^2$ mol^{-2} sec^{-1}. At 0.05 *M* benzaldehyde, the intercept is 0.11 and the slope is 3.60×10^{-2}. From these values we calculate $k_1 = 0.315 \times 10^{-2}$ l. mol^{-1} sec^{-1}, $k_2 = 5.4 \times 10^{-2}$ $l.^2$ mol^{-2} sec^{-1}, and $K_2 = 40$ l. mol^{-1}. Using these values, the observed oxidation rate constant may be calculated from

$$k_{ox} = \frac{k_1[H^+] + k_2K_2[H^+]^2[RCHO]}{1 + K_2[RCHO]}$$

The calculated values are summarized in Table VII, and it can be seen that the agreement is good except for the higher aldehyde concentrations at 0.05 *M* perchloric acid.

The effect of solvent composition on the rate of oxidation was determined giving the data in Table VIII. The effect is surprisingly small considering the great sensitivity of the reaction toward changes in acid concentration. For the perchloric acid concentration used to obtain the data in Table VIII, the Hammett acidity parameter, h_0, increases by a factor of about 3.8 over this solvent range.[7] Since the rates do not increase in the fashion predicted from the second-order acid terms in the rate law, it is apparent that the small effect from changing the reaction medium is the result of opposing influences.

Table VIII. Effect of Changing Solvent Composition on Oxidation Rates[a]

Solvent, % HOAc	$k \times 10^3$, sec^{-1}
81.1	0.35 ± 0.02
87.0	0.55 ± 0.03
91.7	0.68 ± 0.04

[a] $[Ce(IV)] = 0.0053\ M$, $[HClO_4] = 0.08\ M$, μ 0.3, 25°, $[RCHO] = 0.06\ M$.

Substituents attached to the benzaldehyde ring were found to retard the rate of oxidation regardless of the sign of the Hammett σ value (Table IX). Similar decreases in the relative oxidation rate for both substituents were noted for spectrophotometric runs done at 0.30 *M* $[H^+]$. In each case, ϵ_{eq} for the substituted

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(7) K. B. Wiberg and R. J. Evans, *J. Am. Chem. Soc.*, 80, 3019 (1958)

benzaldehyde was greater than that for benzaldehyde suggesting that at least part of the rate reduction was due to decreases in the formation constants for the initial complexes.

Table IX. Oxidation Rates of Substituted Benzaldehydes[a]

Substituent	σ	$k_{ox} \times 10^3$, sec^{-1}
H	0.00	0.34 ± 0.01
4-Cl	0.227	0.157 ± 0.005
4-CH_3	−0.268	0.083 ± 0.023

[a] [Ce(IV)] = 0.0050 *M*, [H^+] = 0.10 *M*, [RCHO] = 0.025 *M*, μ = 0.6, 85% HOAc.

Since a carbon–hydrogen bond is cleaved during the reaction, the kinetic hydrogen isotope effect was examined. Benzaldehyde-*d* was prepared as described previously,[8] and was found to contain 0.988 of a deuterium. With 0.1 *M* perchloric acid, and 0.025 *M* benzaldehyde-*d*, the titrimetric rate constant was 0.026 $\times 10^{-3}$ sec^{-1} and the spectrometric rate constant was 0.023 $\times 10^{-3}$ sec^{-1} giving $k_H/k_D = 16$.

The reaction between benzaldehyde and a one-electron oxidant such as cerium(IV) might be expected to proceed with the intermediate formation of free radicals. In agreement with this, it was found that the oxidation of triphenylacetaldehyde by ceric perchlorate in aqueous acetic acid gave exclusively triphenylcarbinol and carbon monoxide.[9] Richardson also found that the cerium(IV) oxidation of benzaldehyde induced the polymerization of acrylamide whereas in the absence of benzaldehyde, cerium(IV) leads only to very slow polymerization. Induced polymerization of acrylic monomers has been widely applied in systems where free-radical intermediates are possible.[10]

It seemed of importance to determine which species acted as the initiator. If it were the benzoyl radical, each polymer chain should contain one or two benzoyl end groups depending on the mechanism of termination. Thus, the cerium(IV) oxidation of benzaldehyde-^{14}C was carried out in the presence of 0.6 *M* acrylonitrile. The voluminous white precipitate was collected and was purified by dissolving it in dimethylformamide and reprecipitating by adding water. The activity was not changed by the second reprecipitation. The results are summarized in Table X.

Table X. Results of Induced Polymerization Experiments[a]

[$HClO_4$], *M*	[RCHO], *M*	Polymer yield, g	Activity, μCi	% trapped
0.307	0.0182	2.35	0.077	3.0
0.307	0.0092	2.30	0.035	1.4
0.100	0.0180	2.20	0.093	3.6

[a] [Ce(IV)] = 0.005 *M*, μ = 0.6, [acrylonitrile] = 0.6 *M*, 85% HOAc, 25°, total volume = 250 ml, RCHO had 39.0 μCi/g.

Even if one assumes that the yield of polymer from the work-up was as low as 50%, the maximum yield of trapped free radicals is only 7%. Therefore, either Ce(IV) is a much better radical trap than acrylonitrile, only part of the reaction proceeds *via* a radical pathway, or the method of isolation and purification led to loss of a considerable part of lower molecular weight polymer. The last possibility is not unreasonable for cerium(IV) could act as a radical trap and terminate polymerization with a relatively short chain length. It might be noted that the activity of the polymer dropped to half after the first reprecipitation.

In order to determine the fraction of a benzoyl group per monomer chain, the molecular weight distribution of the polymer was determined. The average molecular weight was 48,600, and less than 1% of the polymer had a molecular weight less than 3000. Integrating the product of the benzaldehyde activity (4.1 $\times 10^3$ μCi/mol) and the weight fraction divided by the molecular weight over the molecular weight distribution gave a calculated activity of 0.074 μCi/g. Considering the errors associated with determining the molecular weight distribution, the calculated value is in good agreement with the observed values indicating that each polymer chain has one benzoyl group.

All of the data given above appear consistent with the mechanism

$$T \xrightleftharpoons[k_{-1}]{k_1} 3M$$

$$H^+ + M \xrightleftharpoons[k_{-2}]{k_2} Ce^{4+} + HOR$$

$$Ce^{4+} + R'CHO \xrightleftharpoons[k_{-3}]{k_3} C_1$$

$$C_1 + R'CHO \xrightleftharpoons[k_{-4}]{k_4} C_2$$

$$C_1 + H^+ \xrightarrow{k_5} R'CO\cdot + Ce(III)$$

$$C_2 + 2H^+ \xrightarrow{k_6} R'CO\cdot + Ce(III) + R'CHO$$

$$R'CO\cdot + Ce(IV) \xrightarrow{k_7} R'CO_2H + Ce(III)$$

The kinetic isotope effect indicates steps 5 and 6 to involve rate-determining C–H bond cleavage. The rate constants in the series have been derived and are summarized in Table XI. The last step is presumably a rapid one which follows the rate-determining step, and therefore no information is available concerning its magnitude. However, k_7 must be quite large so that this reaction will be competitive with the capture of the benzoyl radical by acrylonitrile.

Table XI. Summary of Rate Constants for the Ceric Ion Oxidation of Benzaldehyde in 85% Acetic Acid at 25°

Term	Value	Source
k_1	0.64×10^{-2} sec^{-1} (0.1 *M* H^+) 1.21×10^{-2} sec^{-1} (0.3 *M* H^+)	Ref 5
k_{-1}/k_1	7.69×10^6 l.^{2} mol^{-2} (0.1 *M* H^+) 0.383×10^6 l.^{2} mol^{-2} (0.3 *M* H^+)	Ref 5
k_2	0.431 l. mol^{-1} sec^{-1}	Figure 9
k_2/k_{-2}[ROH]	0.185 l./mol	See text
k_{-2}[ROH]$/k_3$	0.123 mol/l.	Figures 8 and 9
k_4/k_{-4}	40 l. mol^{-1}	Figure 10
k_5	0.315 l. mol^{-1} sec^{-1}	Figure 1
k_6	5.4×10^{-2} l.^{2} mol^{-2} sec^{-1}	Figure 10

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[8] K. B. Wiberg, *J. Am. Chem. Soc.*, 76, 5371 (1954).

[9] Unpublished results, W. Richardson, *Cf.* K. B. Wiberg and P. A. Lepse, *ibid.*, **86**, 2612 (1964).

[10] G. Mino, S. Kaizerman, and E. Rasmussen, *ibid.*, 81, 1494 (1959).

The large rate retardation found on the addition of nitrate ion presumably occurs because nitrate ion will compete with the aldehyde in step 3.

Experimental Section

Reagents. All solid inorganic reagents were converted to the anhydrous form before using by heating at 110°. The sodium perchlorate was tested for chloride ion with silver nitrate solution and for chlorate with acidic iodide solution. When either was found, the material was purified by recrystallization from water.

Perchloric acid was reagent grade. Cerium(IV) perchlorate was obtained from the G. F. Smith Chemical Co. as an approximately 0.5 *M* solution in 3 *M* perchloric acid. The ceric ion concentration was determined by titration with sodium thiosulfate solution to a starch–iodine end point. The acid concentration was determined by dissolving samples in acetic acid, adding an excess of acetic anhydride to remove water, and titrating potentiometrically with a standard solution of sodium acetate in glacial acetic acid.

Acetic acid was purified by heating with chromic acid followed by vacuum distillation. The water content was determined spectrometrically using acetic anhydride.[11] Water was purified by distillation from chromic acid.

Benzaldehyde was purified immediately before use by distillation under reduced pressure under a nitrogen atmosphere. A center cut was taken, and was kept under nitrogen. The substituted benzaldehydes were commercial samples. The liquid aldehydes were distilled using the same procedure as for benzaldehyde and the solid aldehydes were recrystallized twice from an ethanol–water mixture and then sublimed at 1 mm at a temperature 10° below their melting point. Benzaldehyde-*d* was prepared as described previously, and was purified in the same fashion as for benzaldehyde. Benzaldehyde-^{14}C was obtained from the New England Nuclear Corp. and was diluted with unlabeled aldehyde to give 3 g of aldehyde having 39.0 μCi/g as determined by liquid scintillation counting.

Solutions. Stock solutions of aqueous acetic acid were prepared gravimetrically in 4-l. quantities taking into account the amount of water present in the acetic acid. Ceric perchlorate solutions in aqueous acetic acid were prepared by weighing samples of the aqueous ceric perchlorate solution, perchloric acid solution, and sodium perchlorate solution into a volumetric flask. Acetic acid was added to compensate for the water in the above solutions, and the flask was filled to the mark with aqueous acetic acid of the correct composition. These solutions were prepared immediately before use because ceric ion slowly oxidizes acetic acid.

Solutions of the aldehydes were prepared by weighing freshly distilled benzaldehyde into a volumetric flask partially filled with solvent. The flask was then filled to the mark with more aqueous acetic acid.

Kinetic Method. Titrimetric runs were made in an apparatus consisting of two flasks joined by a glass U tube. The U tube had a stopcock which could be attached to a vacuum line, and one flask had a semiautomatic pipet. The two solutions were placed in separate flasks and were degassed by a repeated freezing, evacuation, and thawing cycle. After bringing the solutions to the thermostat temperature (25.0°), they were mixed by tilting the assembly. Aliquots were removed *via* the pipet using nitrogen pressure. The solutions were quenched with iodide ion, followed by titration with sodium thiosulfate.

Spectrometric runs were carried out using a two-arm cell which was attached at its center to a rectangular 10-mm reaction cell. The two solutions were placed in separate cells and were degassed. After warming to the thermostat temperature, the cell was inverted and the reaction cell was placed in the light path of a Beckman DU spectrometer. The light path passed through a small water thermostat so that the solution was maintained at 25.0°.

Acknowledgments. We wish to thank Dr. William Richardson for his invaluable assistance in the early phases of this investigation. We also wish to thank Dr. D. W. Kemp and the American Cyanamid Co. for carrying out the determination of the molecular weight of the acrylonitrile polymer *via* gel permeation chromatography.

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(11) S. Bruckenstein, Ph.D. thesis, University of Minnesota, 1952.

The Prevalence of *cis*-Addition Products in the Reaction of the Butenyl Grignard Reagent with Sterically Hindered Ketones

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Abstract: The reactions of crotylmagnesium bromide with ethyl isopropyl, diisopropyl, isopropyl *t*-butyl, and di-*t*-butyl ketones have been examined under carefully controlled conditions. The quantity of α-methylallylcarbinol formed in each case was found to decrease and the amount of crotylcarbinol to increase progressively as the steric requirements of the alkyl groups attached to the carbonyl of the ketone increased. This observation probably reflects increasing steric hindrance in the transition state leading to α-methylallyl products. In all cases, the *cis*/*trans* ratio of the crotyl adducts was greater than unity, which can be explained by invoking the hypothesis that the *cis* form of the butenyl Grignard reagent is more thermodynamically stable than the *trans* form. Several mechanistic possibilities have been proposed to account for the results.

A great deal of work has appeared in the last 23 years concerning the structure and mode of reaction of the butenyl Grignard reagent. One of the more interesting reactions of this species is its facile addition to di-*t*-butyl ketone to give crotyldi-*t*-butylcarbinol in 69% yield.[1] To our knowledge, this still remains as the only example of formation of a product which can be considered as derived from the primary form of the

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[1] K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, 72, 218 (1950).