# Metal-Ion Oxidative Decarboxylations. 9.[1] Reaction of Benzilic Acid with Cerium(IV) in Acidic Perchlorate and Sulfate Media

Samir B. Hanna* and Sezai A. Sarac

*Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65401*

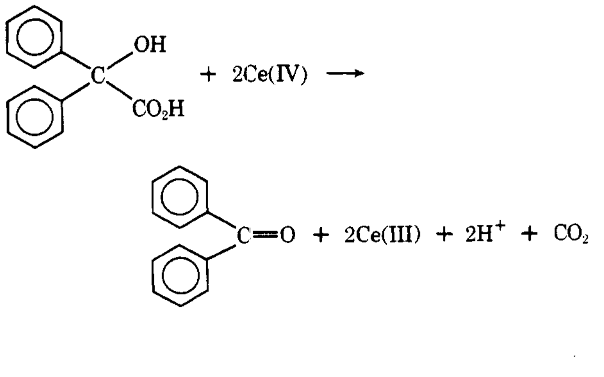
*Received July 27, 1976*

The kinetics of oxidation of benzilic acid (HLH) to benzophenone by cerium(IV) has been studied in several media using the stopped-flow technique. In $HClO_4$–$Na_2SO_4$–$NaClO_4$ media, which allow for the variation and control of the concentrations of the various Ce(IV) species at constant $[H^+]$ and ionic strength, the rate data suggest $CeSO_4^{2+}$ as the kinetically relevant species. In $HClO_4$ the observed first-order rate constants, $k^I_{obsd}$, first increase with increasing HLH concentration, then decrease slightly at higher substrate concentrations suggesting the intermediacy of two complexes: a reactive [Ce(IV)HL] and a $[Ce(IV)(HL)_2]$ which resists reaction. The rate law which best describes the observed kinetics in $HClO_4$ media is given by $-d[Ce^{IV}]_T/dt = k^I_{obsd}[Ce(IV)]_T$, $k^I_{obsd} = (k_\alpha K_7'[HLH] + k_\beta K_7'K_8'[HLH]^2)/(1 + K_7'[HLH] + K_7'K_8'[HLH]^2)$, where $K_7'$ and $K_8'$ are $H^+$-dependent equilibrium constants for the formation of the 1:1 and 1:2 complexes, respectively. The kinetic parameters $k_\alpha$ and $k_\beta$ are the rate constants for the intramolecular redox reaction of the 1:1 and 1:2 complexes, respectively. The rates in $H_2SO_4$ are much slower than those in $HClO_4$ and do not reflect strong complex formation before electron transfer. Whereas $H^+$ had an inhibiting effect in the above-mentioned media, catalysis by $H^+$ was manifest in $HClO_4$–HOAc media, possibly through decreasing acetato complexation of Ce(IV).

In spite of the multitude and variety of reports on the uses of cerium(IV) in mechanistic and synthetic studies,[2,3] the investigations frequently refer to the oxidant as "Ce(IV)" without specifying the particular cerium(IV) species involved in the oxidation. In sulfuric acid, where many kinetic investigations are conducted,[4] cerium(IV) exists mainly as a mixture of several sulfato complexes: $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$.[5] On the other hand, in acidic perchlorate media, cerium(IV) is not complexed, although the following species have been reported:[6,7] $Ce^{4+}$, $CeOH^{3+}$, $Ce(OH)_2^{2+}$, $(CeOCe)^{6+}$, and $(HOCeOCeOH)^{4+}$. In perchloric acid, evidence for polymeric species with molecular weight up to 40 000 has been recently reported.[8] The presence of such species would certainly lead to complications in the kinetic analyses of rate data.[9] Their presence can be tested for by reaction with $H_2O_2$ which, owing to complex formation, gives a red color that fades only slowly.[9] Polymeric species can be avoided, however, by reduction of Ce(IV) to Ce(III) with excess $H_2O_2$ followed by electrochemical oxidation.[9,10] Freshly electrolyzed cerium solutions in $HClO_4$ thus contain only monomeric species whose concentrations are governed by a set of hydrolysis constants.

Recently, we proposed the system $HClO_4$–$Na_2SO_4$–$NaClO_4$ as an ideal acidic sulfate medium in which the various concentrations of all the cerium(IV) species, governed by known equilibrium constants, can be calculated and varied at will.[11] At a specified $[H^+]$ and constant ionic strength, one introduces calculated amounts of $Na_2SO_4$ to generate controllable concentrations of the various cerium(IV) species and then studies the rate of a redox reaction as a function of variations in such species.[11]

The oxidative decarboxylation of benzilic acid to benzophenone (eq 1) was chosen as a model reaction to test the proposed idea of pinpointing the kinetically significant species of cerium(IV). Although the said decarboxylation has been studied previously in some detail,[12,13] the medium was not defined clearly with respect to either $[H^+]$ or the ionic strength. In 1–2.5 M $H_2SO_4$, $Ce(OH)_2^{2+}$ was suggested as the main reactive species.[12] In the present paper we report the results of a spectrophotometric study, mainly by the stopped-flow technique, of the cerium(IV) oxidation of benzilic acid to benzophenone in acidic perchlorate and sulfate media.



(1)

## Experimental Section

**Materials.** Cerium(IV) in perchloric acid was prepared by the electrolytic oxidation of cerium(III) perchlorate solutions.[9–13] The latter were obtained either from ammonium cerium(IV) nitrate (Fisher, Certified A. C. S.) or from cerium(IV) perchlorate solution (G. Frederick Smith Chemical Co.) by reduction with excess $H_2O_2$. The electrolyses were carried out in perchloric acid [ca. 0.02 M Ce(IV) in 4 M $HClO_4$] with a spinning cylindrical Pt-gauze anode and a Pt-wire cathode for 2.5 h. The steps involved in the preparations are summarized in Scheme I. Electrolytically reoxidized cerium solutions in perchloric acid were titrated against ammonium iron(II) sulfate for their Ce(IV) content,[14] and against standardized NaOH for their acid content.

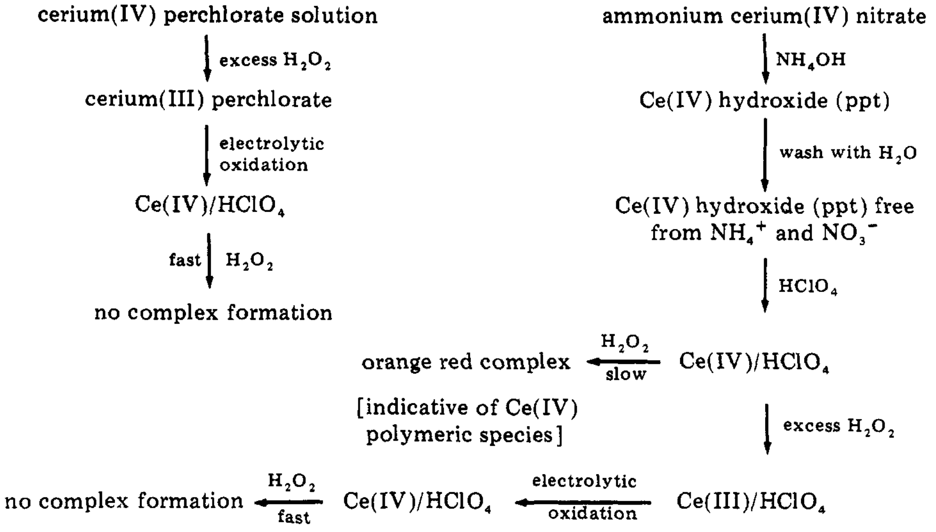
Cerium(IV) in $H_2SO_4$ solutions were prepared freshly before each series of kinetic runs by dissolving cerium(IV) sulfate or ammonium cerium(IV) sulfate (Merck, p.a.) in sulfuric acid solutions; these solutions were standardized by the same method used for cerium(IV) perchlorate and were double checked spectrophotometrically.[15]

Benzilic acid, acrylamide, *N,N′*-methylenebisacrylamide, *N,N,N′,N′*-tetramethylenediamine (TEMED), and diphenylacetic acid were Eastman, White Label chemicals. Lead-free double vacuum-distilled 70% perchloric acid, sodium perchlorate, and ammonium iron(II) sulfate (A. C. S.) were from G. Frederick Smith Chemical Co. Sulfuric acid and sodium sulfate were from Fisher.

**Stoichiometry.** The stoichiometry was determined, under the conditions of kinetic runs, from the absorbance of benzophenone (monitored at 256 nm) produced on the oxidation of a slight excess of benzilic acid by a known amount of Ce(IV). The results point to the consumption of 2 mol of Ce(IV) (monitored at 300 nm) per mol of benzophenone produced (Figure 1). This confirms the stoichiometry previously reported[12,13] and depicted in eq 1.

**Kinetics.** The majority of rate measurements were done on a Durrum-Gibson stopped-flow apparatus equipped with a photometric log amplifier. The signal from the spectrophotometer's photomultiplier was fed into a Biomation transient recorder, Model 802, which was interfaced with a Tektronix storage oscilloscope, a Bausch and Lomb plotter, and a Data Cap tape perforator, Model 820. The digitized data were retrieved from the transient recorder through the tape perforator and were processed by a linear least-squares program of polynomial fit on an IBM 370/168. A typical computer-drawn second-order plot of the data output is shown in Figure 2; the uncertainty

Scheme I



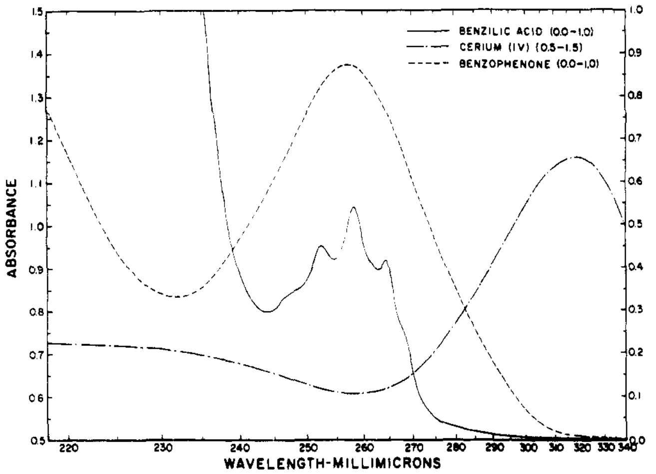


**Figure 1.** Absorption spectra of $2 \times 10^{-4}$ M cerium(IV) in sulfuric acid, $1 \times 10^{-3}$ M benzilic acid, and $5 \times 10^{-5}$ M benzophenone.

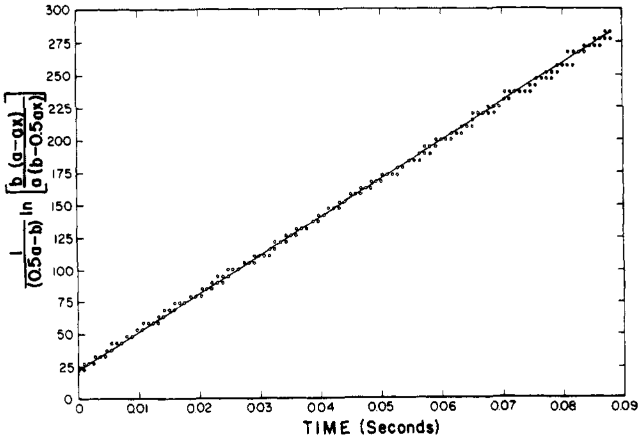


**Figure 2.** Second-order computer plot of cerium(IV) reaction with benzilic acid.

in the slopes of such plots was calculated to be 0.5–1.2%. Straight lines were obtained routinely over 80% reaction and the rate constants were reproducible to better than ±3%. For the slower runs, a Beckman DK-2A spectrophotometer equipped with a time-drive attachment and a thermostated cell holder was used.

For most runs, the benzilic acid concentration was 10–20 times the initial concentration of cerium(IV). The reactions were followed by observing the change in absorbance at 300–320 nm, characteristic of cerium(IV). In several experiments, the rates were followed by monitoring the production of benzophenone at 256 nm.

**Tests for Free Radicals.** Tests for polymerization,[16] as indicated by gel formation, of several monomers were conducted for mixtures of cerium(IV) with benzilic acid, EDTA, malic acid, and oxalic acid. While immediate gel formation was observed with EDTA, neither benzilic acid nor the other acids initiated visible polymerization except after long periods. Mercuric chloride, which has been used as a free-radical trap in similar systems,[17] gave no visible precipitate of $Hg^0$ during the cerium(IV) oxidation of benzilic acid.

## Results and Discussion

We studied the oxidation of benzilic acid with cerium(IV) in four media. Employing electrolytically generated Ce(IV), we used an acidic sulfate medium which consisted of $HClO_4$–$Na_2SO_4$–$NaClO_4$ and an acidic perchlorate medium. The two other media consisted of either cerium(IV) sulfate or ammonium cerium(IV) sulfate in $H_2SO_4$ solutions, and of perchloric–acetic acids mixtures.

**A. Kinetic Identification of the Reactive Cerium(IV) Species in Acidic Sulfate Media.** We chose the system $HClO_4$–$Na_2SO_4$–$NaClO_4$ as an acidic sulfate medium to define $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$, and the ionic strength $\mu$. This system is preferred to sulfuric acid because it has the distinct advantages of ensuring (1) an $[H^+]$ which can be varied independently of the sulfate concentration, while maintaining a defined and constant $\mu$, and (2) a defined and controllable distribution of Ce(IV) species. If one defines $[H^+] = c$, and the formal concentrations of $Na_2SO_4$ and $HClO_4$ as $m$ and $s$, respectively, then $s = c + [HSO_4^-]$, and $[HSO_4^-] = cm/c + K_a$ where $K_a$ is the second dissociation constant for sulfuric acid. Using eq 2 of Reynolds and Fukushima[18]

$$\log K_a = -1.991 + \frac{2.04\sqrt{\mu}}{1 + 1.7\sqrt{\mu}} + 0.0314\mu \qquad (2)$$

to compute the dependence of $K_a$ on $\mu$ in conjunction with the accepted definition of ionic strength, $\mu = \frac{1}{2} \Sigma_i c_i z_i^2$, one calculates the amount of $NaClO_4$ necessary to attain a certain ionic strength in the system $HClO_4$–$Na_2SO_4$–$NaClO_4$ from

$$\mu = \tfrac{1}{2}(c + [HSO_4^-] + 4[SO_4^{2-}] + 2m + s + 2[NaClO_4]) \qquad (3)$$

$$[NaClO_4] = \mu - 3m + s - 2c \qquad (4)$$

Hardwick and Robertson deterined the equilibrium constants, eq 5–7, at $[H^+] = 1$ M and $\mu = 2$ in a range of sulfate ion concentrations from $10^{-3}$ to 0.7 M.[19]

**Table I. First-Order Rate Constants for the Ce(IV)[a]–Benzilic Acid[b] Reaction at 25 °C, $\mu$ = 1.00 ($NaClO_4$)**

| Run | $Na_2SO_4$[c] | $[H^+]$ | $HClO_4$[c] | $NaClO_4$[c] | $Ce(OH)^{3+}$[d] | $Ce(OH)_2^{2+}$[d] | $Ce^{4+}$[d] | CeX[d,e] | $CeX_2$[d,e] | $CeX_3$[d,e] | $k^I_{obsd}$, $s^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.002 | 0.75 | 0.75 | 0.246 | 9.3720 | 1.5000 | 1.0980 | 67.767 | 20.017 | 0.246 | 19.2 |
| 2 | 0.004 | | 0.75 | 0.242 | 4.0830 | 0.6530 | 0.4790 | 59.045 | 34.882 | 0.859 | 17.6 |
| 3 | 0.010 | | 0.76 | 0.229 | 1.0630 | 0.1700 | 0.1250 | 38.415 | 56.736 | 3.491 | 6.4 |
| 4 | 0.020 | | 0.77 | 0.209 | 0.3190 | 0.0510 | 0.0370 | 23.068 | 68.138 | 8.386 | 1.85 |
| 5 | 0.040 | | 0.79 | 0.168 | 0.0830 | 0.0130 | 0.0100 | 11.947 | 70.576 | 17.372 | 0.65 |
| 6 | 0.100 | | 0.85 | 0.044 | 0.0110 | 0.0020 | 0.0010 | 4.022 | 59.406 | 36.557 | 0.14 |
| 7 | 0.002 | 0.50 | 0.50 | 0.496 | 5.9600 | 1.4300 | 0.4660 | 64.246 | 27.411 | 0.487 | 26.1 |
| 8 | 0.004 | | 0.50 | 0.492 | 2.3850 | 0.5720 | 0.1860 | 51.419 | 43.877 | 1.560 | 19.4 |
| 9 | 0.010 | | 0.51 | 0.479 | 0.5540 | 0.1330 | 0.0430 | 29.874 | 63.730 | 5.665 | 5.2 |
| 10 | 0.025 | | 0.52 | 0.448 | 0.0990 | 0.0240 | 0.0080 | 13.284 | 70.844 | 15.743 | 1.42 |
| 11 | 0.100 | | 0.59 | 0.290 | 0.0050 | 0.0010 | 0.0004 | 2.421 | 51.657 | 45.916 | 0.09 |
| 12 | 0.003 | 0.40 | 0.40 | 0.594 | 2.6300 | 0.7890 | 0.1640 | 53.458 | 41.609 | 1.350 | 21.0 |
| 13 | 0.010 | | 0.41 | 0.579 | 0.3790 | 0.1140 | 0.0240 | 25.673 | 66.610 | 7.201 | 8.1 |
| 14 | 0.030 | | 0.43 | 0.537 | 0.0440 | 0.0130 | 0.0030 | 8.838 | 68.792 | 22.311 | 1.34 |
| 15 | 0.100 | | 0.54 | 0.286 | 0.0010 | 0.0003 | 0.0001 | 0.971 | 37.774 | 61.254 | 0.05 |
| 16 | 0.001 | 0.30 | 0.30 | 0.698 | 7.2950 | 2.9180 | 0.3420 | 66.970 | 22.169 | 0.306 | 44. |
| 17 | 0.003 | | 0.30 | 0.694 | 1.7400 | 0.6960 | 0.0820 | 47.923 | 47.591 | 1.970 | 28. |
| 18 | 0.010 | | 0.31 | 0.678 | 0.2280 | 0.0910 | 0.0110 | 20.909 | 69.215 | 9.547 | 9.0 |
| 19 | 0.030 | | 0.32 | 0.636 | 0.0240 | 0.0100 | 0.0010 | 6.647 | 66.006 | 27.312 | 1.61 |
| 20 | 0.100 | | 0.39 | 0.488 | 0.0014 | 0.0005 | 0.0001 | 1.254 | 41.502 | 57.242 | 0.14 |
| 21 | 0.0005 | 0.20 | 0.20 | 0.799 | 9.5910 | 5.7540 | 0.2990 | 68.539 | 15.665 | 0.149 | 55. |
| 22 | 0.002 | | 0.20 | 0.795 | 1.7440 | 1.0460 | 0.0540 | 49.847 | 45.572 | 1.736 | 42. |
| 23 | 0.005 | | 0.20 | 0.788 | 0.3970 | 0.2380 | 0.0124 | 28.359 | 64.819 | 6.173 | 25.6 |
| 24 | 0.020 | | 0.22 | 0.755 | 0.0257 | 0.0154 | 0.0008 | 7.336 | 67.071 | 25.550 | 3.9 |
| 25 | 0.100 | | 0.28 | 0.576 | 0.0005 | 0.0003 | 0.0000 | 0.748 | 34.170 | 65.082 | 0.17 |

[a] $[Ce(IV)]_0 = 2.5 \times 10^{-5}$ M. [b] $[\text{Benzilic acid}]_0 = 5 \times 10^{-4}$ M. [c] Formal concentrations. [d] Percent of total [Ce(IV)]. [e] $X = SO_4^{2-}$.

$$Ce(4) + HSO_4^- \overset{K_1}{\rightleftharpoons} CeSO_4^{2+} + H^+ \tag{5}$$

$$CeSO_4^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \tag{6}$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+ \tag{7}$$

The values of $K_1$, $K_2$, and $K_3$ are 3500, 200, and 20, respectively. Another set of equilibrium constants for the Ce(IV) sulfato complexation was determined by Bächmann and Lieser[20] at $\mu = 5.9$. We calculated their values to be about 8600, 500, and 10, respectively.[21] The symbol Ce(4) in eq 5 represents the nonsulfated Ce(IV) species, $Ce^{4+}$, $CeOH^{3+}$, and $Ce(OH)_2^{2+}$, whose concentrations can be estimated from the hydrolysis constants given by Everett and Skoog,[22] eq 8 and 9. The values of the hydrolysis constants, $K_4$ and $K_5$, determined spectrophotometrically at $\mu = 1$, are 6.4 and 0.12, respectively.[22]

$$Ce^{4+} + H_2O \overset{K_4}{\rightleftharpoons} CeOH^{3+} + H^+ \tag{8}$$

$$CeOH^{3+} + H_2O \overset{K_5}{\rightleftharpoons} Ce(OH)_2^{2+} + H^+ \tag{9}$$

For our work, we needed $K_1$, $K_2$, and $K_3$ at $\mu = 1$. We evaluated these equilibrium constants at $\mu = 1$ in acidic sulfate media ($HClO_4$–$Na_2SO_4$–$NaClO_4$) from spectrophotometric measurements at 400 nm by using the method of Hardwick and Robertson.[19] The values are 2300, 120, and 5, respectively.

The above equilibria, eq 5–9, were solved simultaneously, and the concentration distribution of the different sulfato and hydroxo complexes, as well as $Ce^{4+}$, was computed for a $10^{-3}$ to 0.6 M range of $Na_2SO_4$ concentrations and $[H^+] = 10^{-2}$ to 1.0 M at a fixed ionic strength, $\mu = 1$.

The results of rate measurements on the Ce(IV)–benzilic acid reaction in $HClO_4$–$Na_2SO_4$–$NaClO_4$ media, for which the concentration distribution of the various Ce(IV) species has been computed, are summarized in Table I. The observed first-order rate constants, in $s^{-1}$, were calculated according to

$$k^I_{obsd}t = \ln\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) \tag{10}$$

by least-squares analysis, from spectrophotometric data collected by observing the formation of benzophenone at 256 nm using the stopped-flow technique; $A_0$, $A_t$, and $A_\infty$ refer to the absorbances at the start of reaction, at time $t$, and at infinity, respectively. Inspection of Table I reveals the following facts. (1) At fixed $[H^+]$ and $\mu$, the rate constant decreases steadily with increasing sulfate concentration. This is to be expected in view of the increase in sulfato complexation. The oxidations of organic and inorganic substrates by Ce(IV) are usually much faster in perchlorate than in sulfate media.[10,23,24] This is a reflection of the competition between the $SO_4^{2-}$ and the substrates' ligands for positions in the coordination sphere around the metal ion, particularly if substitution is a necessary prerequisite for electron transfer.[25] An exception to this expectation is found in Adamson, Dainton, and Glentworth's report on the Ce(IV)–Fe(II) redox reaction where catalysis by small concentrations of sulfate was reported.[26] (2) The decreases in the concentrations of $CeOH^{3+}$, $Ce(OH)_2^{2+}$, and $Ce^{4+}$ which accompany the addition of $Na_2SO_4$ are very much greater than the corresponding decreases in $k^I_{obsd}$. (3) At any fixed $[H^+]$ the increases in the concentration of $Ce(SO_4)_3^{2-}$ are accompanied by decreases in $k^I_{obsd}$. (4) Of all the species, whose concentrations are calculable by known equilibrium constants, the monosulfato complex, $CeSO_4^{2+}$, shows the closest parallelism to $k^I_{obsd}$.

The data in Table I were subjected to statistical analysis by a stepwise regression technique.[27] The correlation coefficients for $k^I_{obsd}$ vs. the concentrations of the six Ce(IV) species are listed in Table II. It is evident that the best correlation exists between $k^I_{obsd}$ and $[CeSO_4^{2+}]$. We wish, therefore, to propose the monosulfato complex as the kinetically relevant Ce(IV) species under our experimental conditions. This is to be contrasted with the results of the earlier investigation[12] which portrayed the dihydroxy species, $Ce(OH)_2^{2+}$, as the reactive

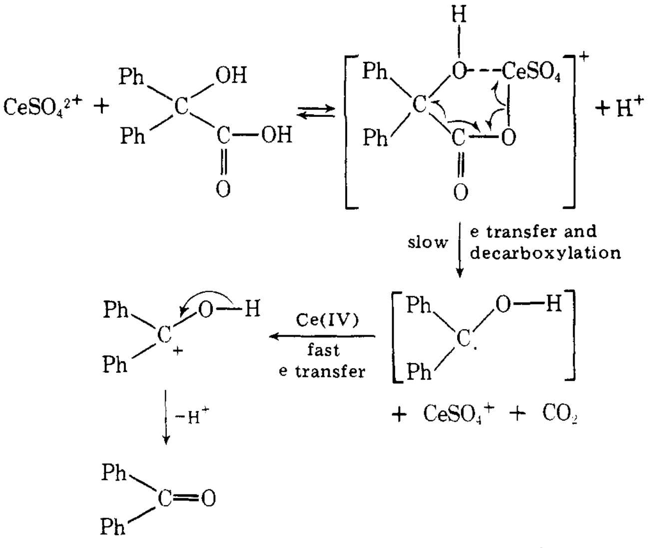
**Table II. Correlation Coefficients for the Observed Rate Constants' Dependence on Ce(IV) Species at Various [H$^+$]**

| | Correlation coefficients for $k^{I}_{obsd}$ vs. | | | | | |
|---|---|---|---|---|---|---|
| [H$^+$], M | Ce(OH)$^{3+}$ | Ce(OH)$_2$$^{2+}$ | Ce$^{4+}$ | CeSO$_4$$^{2+}$ | Ce(SO$_4$)$_2$ | Ce(SO$_4$)$_3$$^{2-}$ |
| 0.20 | 0.80212 | 0.80209 | 0.80156 | 0.99713 | −0.51502 | −0.83096 |
| 0.30 | 0.92180 | 0.92178 | 0.92234 | 0.99472 | −0.71337 | −0.77033 |
| 0.40 | 0.97142 | 0.97153 | 0.97182 | 0.99411 | −0.27878 | −0.74953 |
| 0.50 | 0.94644 | 0.94639 | 0.94605 | 0.97311 | −0.86448 | −0.71084 |
| 0.75 | 0.90823 | 0.90809 | 0.90853 | 0.97147 | −0.95585 | −0.72417 |

species in 1-2.5 M $H_2SO_4$. We must emphasize at this point that the poor correlation coefficient for $k^{I}_{obsd}$ vs. [Ce(OH)$_2$$^{2+}$] indicates a very minor role, if any, for the participation of the dihydroxy species in the oxidative pathway under our conditions. It is much more unlikely that Ce(OH)$_2$$^{2+}$ could be a kinetically significant participant in 1-2.5 M $H_2SO_4$. One calculates that over 99.99% of Ce(IV) in the latter media exists as the trisulfato complex, which is expected to be relatively unreactive toward oxidizable ligands. The rates of oxidation of benzilic acid by Ce(IV) in 1-2.5 M $H_2SO_4$ are quite slow[12] in comparison to the rates reported in this work.

Stepwise regression analysis of the data in Table I gives the following values for the rate constant specific of the monosulfato species: $k_{CeX}$ = 30, 42, 41, 67, and 95 at 0.75, 0.5, 0.4, 0.3, and 0.2 M H$^+$, respectively. The direct and logarithmic relationships of these kinetic parameters to the hydrogen ion concentration in the reaction media are shown in Figure 3. The plot of log $k_{CeX}$ against −log [H$^+$] is a straight line with a slope of 1.03 ± 0.17. This inverse dependence on [H$^+$] may be explained in terms of a transition state which contains the reactants minus an H$^+$.[28] This is compatible with the mechanism shown in Scheme II which portrays preliminary Ce(IV)-benzilic acid complex formation followed by a rate-determining intramolecular electron transfer simultaneous with C-C bond fission and liberation of $CO_2$. The produced radical is expected to be unstable and to lose an electron in a fast step to a second Ce(IV). The proposed mechanism is summarized (HLH = benzilic acid and L′ = benzophenone) in eq 11-14.

Scheme II



$$CeX^{2+} + HLH \underset{fast}{\overset{K_6}{\rightleftharpoons}} [HLCeX]^+ + H^+ \qquad (11)$$

$$[HLCeX] \xrightarrow{slow} HL'\cdot + CeX^+ + CO_2 \qquad (12)$$

$$HL'\cdot + Ce(IV) \xrightarrow{fast} [HL']^+ + Ce(III) \qquad (13)$$

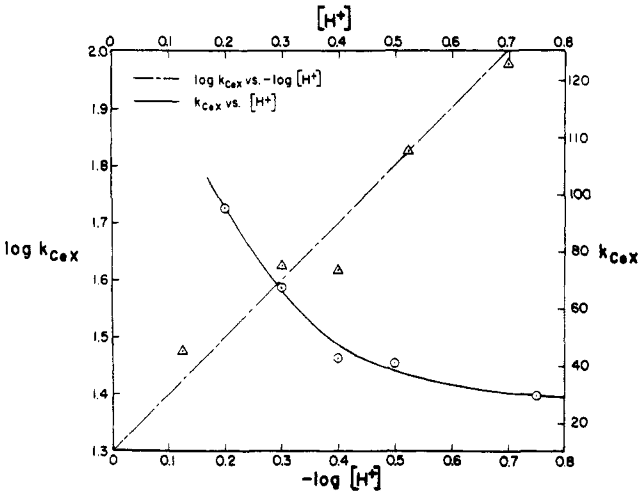


Figure 3. Plots of log $k_{CeX}$ against − log [H$^+$] and of $k_{CeX}$ against [H$^+$] in $HClO_4$-$Na_2SO_4$-$NaClO_4$ media.

$$[HL']^+ \xrightarrow{fast} L' + H^+ \qquad (14)$$

**B. Kinetics in Sulfuric and in Perchloric Acids.** The observed pseudo-first-order and second-order rate constants, $k^{I}_{obsd}$ and $k^{II}_{obsd}$, calculated by eq 10 and 15, respectively, for the reaction of Ce(IV) in aqueous $H_2SO_4$, are listed in Table III.

$$k^{II}_{obsd}t = \frac{1}{(0.5a - b)} \ln\left[\frac{b(a - ax)}{a(b - 0.5ax)}\right] \qquad (15)$$

$$x = (A_0 - A_t)/(A_0 - A_\infty)$$

For a fixed initial concentration of Ce(IV) and at constant acidity, $k^{I}_{obsd}$ increases linearly with increasing [HLH]$_0$. The slope of the straight-line plot of $k^{I}_{obsd}$ against [HLH]$_0$ was found to be 4.63 ± 0.04 M$^{-1}$ s$^{-1}$ by least squares. An average $k^{II}_{obsd}$, calculated by eq 15, is 5.13 M$^{-1}$ s$^{-1}$. By comparison with other organic substrates' oxidations, one might expect a Ce(IV)-benzilic acid complex as an intermediate. Cerium(IV)-organic ligand complex formation appears to depend on the anion associated with Ce(IV). It is generally believed that the presence of sulfate is not conducive to Ce(IV)-organic ligand complex formation. However, there are several cases [ethylene glycol,[29] malonic acid,[2,30,31] mandelic acid,[32] oxalic acid,[33] and diethylenetriaminepentaacetic acid (DTPA)[34]] where such complexation in acidic sulfate media has been documented. A plot of 1/$k^{I}_{obsd}$ against 1/[HLH]$_0$ (Table III) gives a straight line; the slope and intercept yield a value of 45 for the acid-dependent equilibrium constant $K_6'$ of Ce(IV)-benzilic acid complex formation at 1.45 M H$^+$.

By contrast, inspection of the rate data in Table IV for the oxidations carried out in $HClO_4$ media reveals that $k^{II}_{obsd}$ is not constant and that $k^{I}_{obsd}$ changes in a nonlinear fashion with changes in [HLH]$_0$. A similar behavior, namely, a difference in the response of $k^{I}_{obsd}$ to changing the concentration

**Table III. Observed Rate Constants in Sulfuric Acid for Different Initial Concentrations of Benzilic Acid at 25 °C, $[H^+] = 1.45$ M, $\lambda = 320$ nm, $[Ce(IV)] = 1.25 \times 10^{-4}$ M**

| Run | $10^3$[benzilic], M | $10^2 k^I_{obsd}$, s$^{-1}$ | $k^{II}_{obsd}$, M$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 254 | 1.25 | 0.68 | 5.71 |
| 255 | 2.50 | 1.24 | 5.07 |
| 258 | 3.12 | 1.54 | 5.15 |
| 256 | 3.75 | 1.90 | 5.03 |
| 257 | 4.37 | 2.17 | 5.02 |
| 259 | 5.00 | 2.37 | 4.79 |

**Table IV. Observed First- and Second-Order Rate Constants and Calculated First-Order Rate Constants in Perchloric Acid for Different Initial Concentrations of Benzilic Acid at 25 °C, $\lambda = 295$ nm at 0.195 and 0.5 M $H^+$ [a]**

| Run | $[H^+]$, M | $10^3$[benzilic], M | $k^I_{obsd}$, s$^{-1}$ | $k_{calcd}$, s$^{-1}$ | $10^{-3} k^{II}_{obsd}$, M$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 342 | 0.195 | 0.50 | 55 | 66 | 126 |
| 343 | | 1.25 | 77 | 84 | 66 |
| 337 | | 2.50 | 92 | 82 | 38 |
| 338 | | 3.13 | 87 | 82 | 25 |
| 339 | | 3.75 | 86 | 82 | 23 |
| 340 | | 4.38 | 84 | 80 | 20 |
| 242 | | 5.00 | 80 | 81 | 16 |
| 353 | 0.50 | 0.50 | 42 | 42 | 91 |
| 354 | | 2.50 | 72 | 73 | 29 |
| 355 | | 3.75 | 73 | 77 | 20 |
| 356 | | 5.00 | 66 | 78 | 13 |

[a] $[Ce(IV)] = 2.5 \times 10^{-4}$ M at $[H^+] = 0.195$ M, and $1.25 \times 10^{-4}$ M at $[H^+] = 0.50$ M.

of the reducing substrate in sulfate and perchlorate media, was observed in a study of the oxidation of glycerol by cerium(IV),[35] and is probably due to the greater availability of Ce(IV) in perchlorate than in sulfate media for complex formation with reducing substrates.

The nonlinear behavior of $k^I_{obsd}$ as a function of changing the initial concentration of benzilic acid in $HClO_4$ media is suggestive of extensive Ce(IV)–HLH complex formation. A plot of the data in Table IV, at 0.195 M $HClO_4$, as $1/k^I_{obsd}$ against $1/[HLH]_0$ is shown in Figure 4. Linearity is obtained only at the lower benzilic acid concentrations. Actually, an increase in $[HLH]_0$ beyond 0.0025 M leads to a decrease in the reaction rate. This behavior may be explained in terms of a Ce(IV)–substrate complex which either resists oxidation or does so very slowly. Since we assume that the 1:1 complex is that which is involved in the observed oxidation (cf. Scheme II), the inert or relatively unreactive complex is probably a 1:2 Ce(IV)–benzilic acid complex. Similar behavior, namely, a decrease in the reaction rate with increasing substrate concentration, has been reported by Littler and Waters for the oxidation of ethanol,[36] by Duke and Forist for the oxidation of butane-2,3-diol,[37] and by Wiberg and Ford for the oxidation of benzaldehyde.[38]

The data in $HClO_4$ then suggest the mechanism summarized in eq 16–19.

$$\text{Ce(IV)} + \text{HLH} \overset{K_7}{\rightleftharpoons} [\text{Ce(IV)HL}] + \text{H}^+ \tag{16}$$

$$[\text{Ce(IV)HL}] + \text{HLH} \overset{K_8}{\rightleftharpoons} [\text{Ce(IV)(HL)}_2] + \text{H}^+ \tag{17}$$

$$[\text{Ce(IV)HL}] \xrightarrow[\text{rate determining}]{k_\alpha} \text{HL}'\cdot + \text{Ce(III)} + \text{CO}_2 \tag{18}$$

$$[\text{Ce(IV)(HL)}_2] \xrightarrow[\text{very slow}]{k_\beta} \text{HL}'\cdot + [\text{Ce(III)HL}] + \text{CO}_2 \tag{19}$$

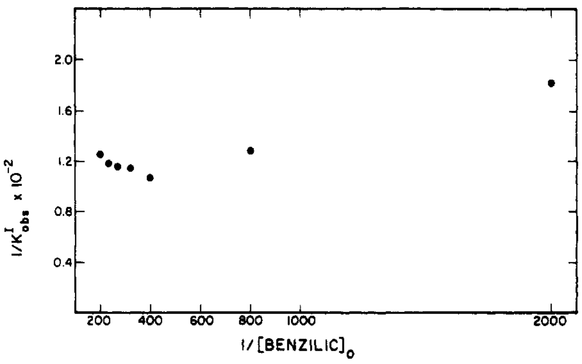


**Figure 4.** Plot of $1/k^I_{obsd}$ against 1/[benzilic] at 0.195 M $H^+$.

From the above equations, the rate of loss of total cerium(IV) in the presence of excess benzilic acid may be expressed as

$$\text{rate} = -\frac{d[\text{Ce(IV)}]_T}{dt} = k^I_{obsd}[\text{Ce(IV)}]_T = k_\alpha[\text{CeHL}] + k_\beta[\text{Ce(HL)}_2] \tag{20}$$

$$[\text{Ce(IV)}]_T = [\text{Ce(IV)}]_{free} + [\text{CeHL}] + [\text{Ce(HL)}_2] = [\text{Ce(IV)}]_{free}\{1 + K_7'[\text{HLH}] + K_7'K_8'[\text{HLH}]^2\} \tag{21}$$

where

$$K_7' = K_7/[H^+] \quad \text{and} \quad K_8' = K_8/[H^+]$$

$$k^I_{obsd} = \frac{k_\alpha K_7'[\text{HLH}] + k_\beta K_7'K_8'[\text{HLH}]^2}{1 + K_7'[\text{HLH}] + K_7'K_8'[\text{HLH}]^2} \tag{22}$$

With the assumption that $K_7' \ll K_8'$, $k_\alpha \gg k_\beta$, and that at relatively low benzilic acid concentrations only the 1:1 complex need be considered, eq 22 may be simplified to

$$k^I_{obsd} = \frac{k_\alpha K_7'[\text{HLH}]}{1 + K_7'[\text{HLH}]} \tag{23}$$

Evaluation of the rate and equilibrium parameters in eq 23 from the linear portions of the plots of $1/k^I_{obsd}$ against $1/[HLH]_0$ is not recommended when the plots are not linear (cf. Figure 4). We, therefore, employed eq 24

$$1/k^{II}_{obsd} = \frac{[\text{HLH}]}{k_\alpha} + \frac{1}{k_\alpha K_7'} \tag{24}$$

for processing the data at 0.195 M $H^+$. A plot of $1/k^{II}_{obsd}$ against $[HLH]_0$ yields a straight line. From the slope and intercept, values of about 4500 for $K_7'$ and 95 s$^{-1}$ for $k_\alpha$ are obtained. Whereas $k_\alpha$ should be independent of the acidity, $K_7'$ is not a true equilibrium constant and should vary with $[H^+]$. This is a consequence of the fact that any of the Ce(IV) species, $Ce^{4+}$, $CeOH^{3+}$, or $Ce(OH)_2^{2+}$, may be involved in the complex formation. The concentrations of such species are governed by $[H^+]$ as shown in eq 8 and 9.

The true equilibrium constant, $K_7$, may be obtained by multiplying $K_7'$ with $[H^+] = 0.195$. This yields a value of about 870. Furthermore, differentiation of eq 23, $\partial k^I_{obsd}/\partial[HLH]_0$, yields an expression, eq 25, from which $K_8 \approx 7$.

$$K_7'K_8' = \frac{1}{[\text{HLH}]^2_{max}} \tag{25}$$

$[HLH]_{max}$ = benzilic acid concentration which corresponds to a maximum in the observed reaction rate

Substitution in eq 22 with $K_7 = 870$, $K_8 = 7$, $k_\alpha = 95$, and $k_\beta = 20$ yields the $k^I_{calcd}$ listed in Table IV. The agreement with $k^I_{obsd}$ is far better at 0.195 M $H^+$ than at 0.5 M $H^+$. It is noteworthy that better agreement between $k^I_{calcd}$ and $k^I_{obsd}$ is obtained when the rate and equilibrium parameters, extracted from the plots of $1/k^I_{obsd}$ against $1/[HLH]_0$, are used.

**Table V. Observed Rate Constants in Various Perchloric Acid Concentrations at 25 °C, [Ce(IV)] = $2.5 \times 10^{-5}$ M, [Benzilic] = $5 \times 10^{-4}$ M, λ = 256 nm**

| Run | $[HClO_4]$, M | $k_{obsd}$, $s^{-1}$ |
|---|---|---|
| 92 | 0.25 | 51 |
| 93 | 0.50 | 48 |
| 94 | 1.00 | 33 |
| 95 | 2.00 | 26 |

**Table VI. Rate Constants in 49.5 wt % Acetic Acid–Perchloric Acid at 25 °C, [Benzilic] = $5 \times 10^{-3}$ M, [Ce(IV)] = $2.5 \times 10^{-4}$ M, λ = 310 nm**

| Run | $[HClO_4]$, M | $k_{obsd}$, $s^{-1}$ | $10^{-2}k_2$, $M^{-1}\,s^{-1}$ |
|---|---|---|---|
| 222 | 0.195 | 15.8 | 32 |
| 223 | 0.425 | 26.3 | 53 |
| 224 | 0.660 | 38 | 77 |
| 225 | 0.890 | 40 | 81 |

The large value of $K_7$ obtained in this work, in comparison to $K = 20$ for the Ce(IV)–glycerol complex in 0.5 M $HClO_4$,[35] and to $K = 18$ and 29 for Ce(IV)–*cis*-1,2-cyclohexanediol and Ce(IV)–*trans*-1,2-cyclohexanediol complexes, respectively,[39] and to our own value of $K_6' = 45$ in 1.45 M $H^+$ in sulfuric acid, indicates very strong complexation in $HClO_4$ media. It is noteworthy that our attempts to detect complex formation in $HClO_4$ by stopped-flow techniques and by rapid scan spectrometry were not successful. The overall reduction of Ce(IV) by benzilic acid in $HClO_4$ media is quite fast, with half-lives in the millisecond region. Presumably, complex formation is even faster than that. Amjad and McAuley report that the Ce(IV)–malic acid complex was formed on mixing (2 ms).[24] This prompts us to question the validity of the spectral information about a presumed 1:1 Ce(IV)–HLH complex which was reported by Grover and Gupta.[12] The presumed complex was shown to have a maximum at 255 nm 10 s after mixing the reactants. The spectrum reported by Grover and Gupta has all the characteristics of benzophenone (Figure 1).

**C. Influence of Acidity.** In $HClO_4$–$Na_2SO_4$–$NaClO_4$ (Table I), $H_2SO_4$,[12,40] and $HClO_4$ (Table V) media, $k^{I}_{obsd}$ decreases with increasing acidity. The order in $[H^+]$ is medium dependent. In the media where $CeSO_4^{2+}$ is clearly the predominantly reactive species, an order of about −1 is observed. In $H_2SO_4$ media doped with $HClO_4$, inverse first-order dependence on $[H^+]$ is reported.[12] In $H_2SO_4$ media, an order of −1.83 is observed.[40] This is possibly due to the interplay of several factors, of which the acid-dependent concentration of the sulfato species is an important one. In $HClO_4$, an order of about −0.34 is calculated from the data in Table V. The inhibiting effect of $H^+$ in all these media can be understood in terms of the mechanism depicted in Scheme II, where complex formation, which is attended by $H^+$ release, would be checked by increasing $[H^+]$. The fractional negative order observed in $HClO_4$ could be due to opposing factors. On the one hand, there is the inhibition of complex formation. On the other, increasing acidity should produce less hydrolyzed, and presumably more reactive, Ce(IV) species.[23] This is tantamount to catalysis by $H^+$.

A case of clear-cut catalysis by $H^+$ is presented in Table VI which contains the rate data obtained in 49.5 wt % acetic acid–perchloric acid solvent mixture. Here, increasing acidity brings about an enhancement in $k^{I}_{obsd}$; the order in $[H^+]$ is about 0.64. We believe that this rate enhancement is again concordant with the mechanism depicted in Scheme II. Cerium(IV) is expected to form relatively stable acetato complexes;[41] their tendency to form [Ce(IV)–HLH] is likely to be lower than that of noncomplexed Ce(IV). When formed, the complex is likely to be a mixed-ligand complex which again may retard electron transfer from HL to Ce(IV) because of stabilization of the latter by the acetate ligands. Increasing acidity would provide $H^+$ to compete with Ce(IV) for the acetate ligands, thereby freeing the complex of their stabilizing influence and hence the rate enhancement.

**Acknowledgment.** The authors express their gratitude to Professors G. L. Bertrand and B. Poling (Rolla) for helpful discussions and to Professor H. Dahn (Lausanne) for hospitality accorded S.B.H. during sabbatical at which time this work was initiated. We wish also to thank the Turkish Government for financial support for S.A.S.

**Registry No.**—Cerium(IV) perchlorate, 14338-93-3; cerium(IV) sulfate, 13590-82-4; benzilic acid, 76-93-7.

## References and Notes

(1) Part 8: S. B. Hanna, R. R. Kessler, A. Merbach, and S. Ruzicka, *J. Chem. Educ.*, **53**, 524 (1976). Results relating to portions of this work have been presented at the 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 24–29, 1975, The First Chemical Congress of the North American Continent, Mexico City, Mexico, Nov 30–Dec 5, 1975, and the 12th Midwest Regional Meeting of the American Chemical Society, Kansas City, Kans., Oct 28–29, 1976.

(2) Jing-Jer Jwo and R. M. Noyes, *J. Am. Chem. Soc.*, **97**, 5422 (1975).

(3) T. L. Ho, *Synthesis*, 347 (1973); G. Galliani, B. Rindone, and C. Scolastico, *Synth. Commun.*, **5**, 319 (1975).

(4) D. Benson, "Comprehensive Chemical Kinetics", Vol. 7, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1972, p 243.

(5) A. McAuley, *Coord. Chem. Rev.*, **5**, 245 (1970).

(6) M. S. Sherrill, C. B. King, and R. C. Spooner, *J. Am. Chem. Soc.*, **65**, 170 (1943).

(7) L. J. Heidt and M. E. Smith, *J. Am. Chem. Soc.*, **70**, 2476 (1948).

(8) K. P. Lowrier and T. Steemers, *Inorg. Nucl. Chem. Lett.*, **12**, 185 (1976).

(9) A. Samuni and G. Czapski, *J. Chem. Soc., Dalton Trans.*, 487 (1973).

(10) M. Ardon and G. Stein, *J. Chem. Soc.*, 104 (1956).

(11) S. B. Hanna, R. R. Kessler, A. Merbach, and S. Ruzicka, *J. Chem. Educ.*, **53**, 524 (1976).

(12) V. K. Grover and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, **31**, 1403 (1969).

(13) S. K. Misra and R. C. Mehrotra, *J. Indian Chem. Soc.*, **44**, 927 (1967).

(14) A. I. Vogel, "Quantitative Inorganic Analysis", 3rd ed, Longman, London, 1961, p 319.

(15) A. I. Medalia and B. J. Byrne, *Anal. Chem.*, **23**, 453 (1951).

(16) B. J. Davis, *Ann. N.Y. Acad. Sci.*, **2**, 121 (1964).

(17) Y. Pocker and B. C. Davis, *J. Am. Chem. Soc.*, **95**, 6216 (1973).

(18) L. Reynolds and S. Fukushima, *Inorg. Chem.*, **2**, 117 (1963).

(19) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

(20) K. Bächmann and K. H. Lieser, *Ber. Bunsenges. Phys. Chem.*, **67**, 810 (1963).

(21) The values given by Bächmann and Lieser[20] are based on a $K_a$ for $HSO_4^-$ = 0.071; we have used a value of 0.1446, extrapolated from Reynolds and Fukushima[18] to $\mu = 5.9$.

(22) K. G. Everett and D. A. Skoog, *Anal. Chem.*, **43**, 1541 (1971).

(23) S. B. Hanna, W. R. Carroll, S. Attiga, and W. H. Webb, *Z. Naturforsch. B*, **30**, 409 (1975).

(24) Z. Amjad and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 2521 (1974).

(25) E. Chaffee and J. O. Edwards, "Inorganic Reaction Mechanisms—Progress in Inorganic Chemistry", Vol. 13, J. O. Edwards, Ed., Interscience, New York, N.Y., 1970.

(26) M. G. Adamson, F. S. Dainton, and P. Glentworth, *Trans. Faraday Soc.*, **61**, 689 (1965).

(27) J. Service and J. H. Goodnight, "A User's Guide to the SAS", North Carolina University, 1972, p 127.

(28) R. P. Bell, "The Proton in Chemistry", Cornell University, Press, Ithaca, N.Y., 1959.

(29) A. A. Katai, V. K. Kulschrestha, and R. H. Marchessault, *J. Phys. Chem.*, **68**, 522 (1964).

(30) K. K. Sengupta and S. Aditya, *Z. Phys. Chem.* (*Frankfurt am Main*), **38**, 25 (1963).

(31) G. J. Kasperek and T. C. Bruice, *Inorg. Chem.*, **10**, 382 (1971).

(32) K. K. Sengupta, S. Aditya, and B. N. Ghosh, *J. Indian Chem. Soc.*, **40**, 823 (1963).

(33) Y. A. El-Tantawy and G. A. Rechnitz, *Anal. Chem.*, **36**, 1774, 2361 (1964).

(34) S. B. Hanna and R. K. Hessley, *Inorg. Nucl. Chem. Lett.*, **7**, 83 (1971).

(35) G. G. Guilbault and W. H. McCurdy, *J. Phys. Chem.*, **67**, 283 (1963).

(36) J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 2767 (1960).

(37) F. R. Duke and A. A. Forist, *J. Am. Chem. Soc.*, **71**, 2790 (1949).

(38) K. B. Wiberg and P. C. Ford, *J. Am. Chem. Soc.*, **91**, 124 (1969).

(39) H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, **32**, 556 (1967).

(40) S. B. Hanna and S. A. Sarac, *J. Org. Chem.*, following paper in this issue.

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