Experimental Section

The CD measurements were made on a Cary-6001 attachment on a Cary-60 spectropolarimeter and uv measurements on a Cary 16 spectrophotometer. The solvents used were spectrograde and were dried over molecular sieves type 4A overnight.

Chloroform was made ethanol free by shaking four times in a separatory funnel with water, drying over sodium sulfate, and passing through a column of aluminum oxide (Wöhrlm, neutral). All measurements were performed by taking volumetric samples from a premixed stock solution and mixing them immediately prior to measurements of spectra. It was found that atmospheric moisture has deleterious effects on the intensity of the spectra and hence, if more than one sample is to be mixed and measured, it is advantageous to do so in a nitrogen atmosphere.

The concentration studies were also mixed under a stream of dry nitrogen.

Pr(dpm)₃. $Pr(dpm)_3$ was prepared according to the literature:[16] yield 82%; mp 219–222° (uncorr); sublim 183° (0.1 mm).

The following are two examples of typical measurements. Case 1: 5α-Cholestane-2β,3β-diol (0.2 mg, entry **4**) was dissolved in 5 ml of a 1.0×10^{-4} M solution of $Pr(dpm)_3$ in dry CCl_4, $\Delta\epsilon_{311}$ +9.7. Case 2: Ponasterone A 20,22-acetonide (0.5 mg) was dissolved in 5 ml of dry CCl_4; 2.5 ml of this was diluted to 5 ml with CCl_4, and the spectrum was taken. The remaining sample was diluted to 5 ml by the addition of 2.5 ml of a 2.0×10^{-4} M solution of $Pr(dpm)_3$ in dry CCl_4, and the spectrum was taken. The difference of the two curves gave the induced CD, $\Delta\epsilon_{312}$ −5.3.

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Oscillations in Chemical Systems. IX.[1] Reactions of Cerium(IV) with Malonic Acid and Its Derivatives

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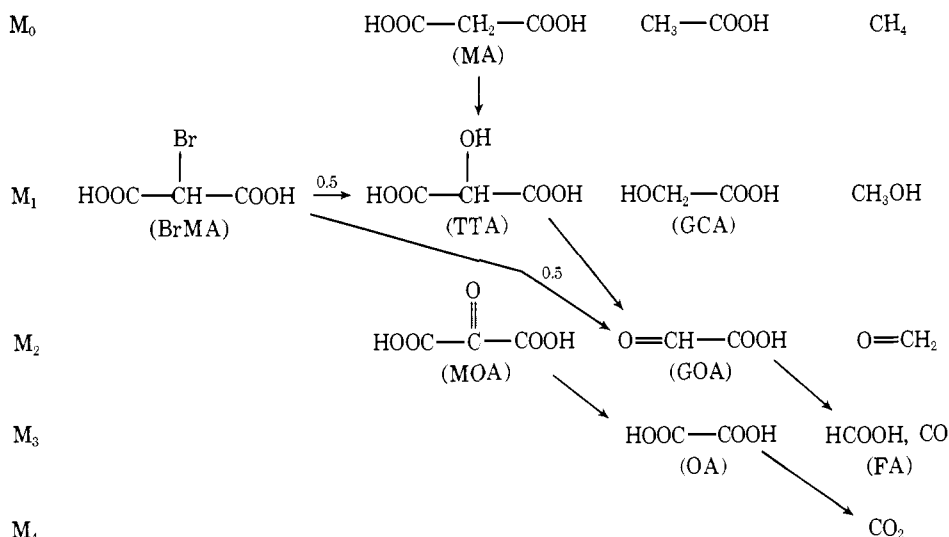
Abstract: Cerium(IV) in 0.8 M H_2SO_4 will oxidize malonic (MA), tartronic (TTA), and glyoxylic (GOA) acids to produce one molecule of formic acid (FA) per molecule of acid. Mesoxalic (MOA) and oxalic (OA) acids are oxidized entirely to carbon dioxide. The sequence of oxidation of malonic acid is apparently MA → TTA → GOA → FA; mesoxalic, oxalic, and glycolic (GCA) acids are not formed as intermediates in significant amounts. Mesoxalic, glyoxylic, and oxalic acids have carbonyl groups adjacent to carboxyl groups and can form five-member chelate rings; they are oxidized within a couple of minutes or less at 25°. Malonic, bromomalonic (BrMA), and tartronic acids have two carboxyl groups separated by an incompletely oxidized carbon atom and can form six-member chelate rings; they are oxidized at 25° at rates approximately consistent with second-order kinetics and rate constants of the order of 1 M^{-1} sec^{-1}. Glycolic and formic acids and formaldehyde are inert to oxidation by cerium(IV) in sulfuric acid even though such oxidation is thermodynamically favored. Bromide ion catalyzes the oxidation of formic acid by cerium(IV); the mechanism involves oxidation of the formic acid by Br_2 or by HOBr. When bromomalonic acid is oxidized by cerium(IV), the rate of consumption of oxidant during a specific run will increase virtually discontinuously by a factor that is often of the order of 2 to 3 and may be as great as 7; production of bromide ion follows a smooth curve through this break point in Ce(IV) consumption. Radicals formed by Ce(IV) attack on several of these molecules are more likely to disproportionate with other radicals than to react with additional Ce(IV) ions. Radicals from the initial oxidation of bromomalonic acid are hydrolyzed to produce bromide ion before they react further. Malonic acid is not significantly attacked by radicals from other organic species, but malonyl radicals can abstract hydrogen from bromomalonic, tartronic, and perhaps glyoxylic acids. Radicals from oxidation of other species can also attack bromomalonic acid thereby initiating liberation of bromide ion. In the presence of bromide ion and cerium(IV), malonyl radicals are converted to bromomalonic acid. In the Ce(IV) + MA + BrMA and Ce(IV) + MA + Br⁻ systems, concentrations of bromide ion can go through peculiar maxima, minima, and stationary conditions that are not entirely explained. The combination of all of these observations permits an unexpectedly complete description of the complicated sequence of events during the cerium(IV) oxidation of malonic and bromomalonic acids.

The best established examples of homogenous chemical oscillators belong to a reaction type first reported by Belousov.[3] Zhabotinskii[4] has subsequently shown that oscillations take place in many solutions containing sulfuric acid, bromate ion, a one-equivalent redox couple with a reduction potential of about 1.0 to 1.5 V, and an organic compound that can be brominated by an enolization mechanism. Many of the subsequent studies have used the Ce(III)–Ce(IV) couple and malonic acid.

The principal features of the mechanism have been eluci-

Chart I

M_0 HOOC—CH_2—COOH CH_3—COOH CH_4
(MA)

M_1 HOOC—CH—COOH $\xrightarrow{0.5}$ HOOC—CH—COOH $HOCH_2$—COOH CH_3OH
     (Br)   (BrMA)   (OH) (TTA)   (GCA)

M_2 HOOC—C—COOH (O)   O=CH—COOH   O=CH_2
     (MOA)   (GOA)

M_3 HOOC—COOH   HCOOH, CO
     (OA)   (FA)

M_4 CO_2

dated by Field, Körös, and Noyes.[5] Bromide ion is consumed by reducing bromate to bromine and hypobromous acid which then brominate the malonic acid. When bromide ion concentration drops below a critical value, bromous acid is formed autocatalytically and initiates bromate oxidation of cerium(III) with formation of cerium(IV) and hypobromous acid. The resulting cerium(IV) oxidizes bromomalonic acid with formation of bromide ion at a rate sufficient to again inhibit the process that oxidizes cerium(III). The basic validity of the mechanism has been substantiated by computations both with a simplified model[6] and with the best available estimates of rate constants for the full mechanism[7].

A key process during the reaction is the oxidation of organic species by cerium(IV) with formation of bromide ion. The work described here was undertaken to obtain more information about the detailed mechanisms of these oxidations by cerium.

Formulation of Problem

A total of 8 equiv are required to oxidize malonic acid (MA) to carbon dioxide. The conceivable intermediates containing an even number of electrons are presented in Chart I. The horizontal lines, designated M_0 to M_4, each differ by 2 equiv, and vertical columns involve the same total number of carbon atoms. Species subsequently shown to be of potential mechanistic interest are designated by abbreviations used below. Bromomalonic acid (BrMA) is considered an M_1 species if the bromine is removed as bromide ion. The significance of the arrows in Chart I will be discussed later.

Because the only known oxidation states of cerium are Ce(III) and Ce(IV), oxidation of a species M_0 to M_3 to form a species on the next line will presumably involve free radical intermediates designated R_0 to R_3, respectively. Mechanistic possibilities are obviously very complex, and detailed elucidation is impossible at the present level of chemical sophistication. However, extensive studies with several of the species in Chart I have permitted us to draw a number of mechanistic inferences. The work has involved almost 400 individual kinetic runs and cannot be presented in detail in this manuscript. Subsections under Results and Discussion are designated with serial capital letters to facilitate cross reference, and enough material is provided so the argument can be followed with this manuscript alone. Many statements assert facts for which no quantitative justification is provided here, but references indicate where

such justification is provided in Dr. Jwo's thesis.[2] Some additional information obtained since completion of the thesis is available as supplemental material as described at the end of this manuscript.

Experimental Section

Materials. Reagent grade potassium bisulfate, $KHSO_4$, was recrystallized twice before use; all other inorganic substances were reagent grade materials used without further purification.

Glycolic acid (GCA), oxalic acid (OA), formic acid (FA), and formaldehyde were commercially available reagent grade chemicals used without further purification. Malonic acid (MA) was usually used without further treatment, but the same results were obtained with material that had been recrystallized from 1:1 acetone-benzene.

Monobromomalonic acid (BrMA) was prepared by brominating an ether solution of malonic acid.[8,9] The crude product was recrystallized two or three times from anhydrous trifluoroacetic acid and stored over soda lime and Drierite. The crystals melted at 111–113° with evolution of carbon dioxide. The content of positive bromine was determined by treating with an excess of aqueous potassium iodide and titrating the resulting iodine with standard thiosulfate solution; this method usually indicated 96–97% purity.

Dibromomalonic acid (Br_2MA) was also prepared from malonic acid by more vigorous bromination in aqueous HBr.[8] The crystals were separated by suction, washed with a little water, and stored over soda lime and Drierite. They melted at 145–147° with evolution of carbon dioxide, and iodometric analysis indicated the dibromomalonic acid was 97% pure.

The sodium salt of tartronic acid (TTA) was prepared by hydrolysis of monobromomalonic acid (BrMA) as suggested by Conrad and Reinbach.[8] The bromoacid was dissolved in cold 9 M sodium hydroxide and heated to over 90° on a water bath for 2–3 hr. The resulting crystals were separated by suction and washed with a little water. They were shaken with dilute acetic acid, separated again by suction, and stored over Drierite. A weighed sample of the sodium salt was converted to the barium salt, and the weight change indicated 97% purity. Because of this satisfactory result, the preparation was not subjected to elementary analysis at that time. It subsequently became apparent from consideration of the stoichiometric observations that this material must have been impure, and a combustion analysis of another preparation revealed only about 63% of the carbon that should have been present. Apparently the sample was contaminated with inorganic matter; the observations could be rationalized by a mixture of sodium hydroxide and sodium carbonate.

The sodium salt of mesoxalic acid (MOA) was prepared by sodium hydroxide hydrolysis of dibromomalonic acid (Br_2MA) by the method of Conrad and Reinbach.[8] The resulting hydrate was presumably[10] $Na_2C(OH)_2(CO_2)_2$. The weight change on conversion to the barium salt indicated a purity of 96–97%, but subsequent el-

emental analysis indicated about 13.5% of inert inorganic impurity.

Glyoxylic acid (GOA) was prepared[11,12] by reducing aqueous oxalic acid with powdered magnesium. A portion of the filtrate was shown with calcium ion to be free of oxalate, and barium glyoxylate was precipitated, washed, and treated with aqueous sulfuric acid. After the resulting barium sulfate had been removed by filtration, the filtrate was concentrated by storage over concentrated sulfuric acid. The resulting crystals were separated, washed with a little water, and stored over Drierite. They melted at 98° with decomposition.

Apparatus and Procedures. Most reactions were followed by determining concentrations of bromide ion and of cerium(IV). Bromide ion was followed potentiometrically with an Orion Model 94-35 bromide ion activity electrode. The apparatus has been described more fully (thesis[2] pp 19-21). Because the potential depended upon the concentration of sulfuric or perchloric acid, the apparatus was calibrated with standard bromide solutions for each acid concentration used. Logarithm of bromide ion concentration was a linear function of potential between 10^{-5} and 10^{-3} M but showed a slight curvature at lower concentrations.

Both spectrophotometric and titrimetric procedures were used to determine cerium(IV) concentration. Titrations were carried out with freshly prepared standard 0.05 M ferrous ammonium sulfate with Ferroin (phenanthroline complex of ferrous ion) as indicator. Tests with known Ce(IV) concentrations gave excellent results.

Spectrophotometric measurements were made with a Beckman DU instrument with thermostated cell compartment. The first measurement in a kinetic run could be made within about 30 sec after the solutions had been mixed, and reactions were usually followed about 90% of the way to completion. Runs in 0.8 M H_2SO_4 were usually followed at 390 nm where the molar extinction coefficient is 1380 M^{-1} cm^{-1}, although some runs at high concentration were followed at 444 nm and a molar extinction coefficient of 150 M^{-1} cm^{-1}. Runs in 0.8 M $HClO_4$ were usually followed at 320 nm where the molar extinction coefficient is 1210 M^{-1} cm^{-1}.

Spectrophotometric behavior of cerium(IV) is strongly dependent upon medium, and addition of 0.01 M H_2SO_4 can approximately double the absorbance of a solution in 0.8 M $HClO_4$ (thesis[2] Figure 2). However, the absorbance in a particular medium obeyed Beer's law excellently at concentrations of Ce(IV) below 10^{-3} M (thesis[2] Figures 3 and 4). At least in sulfuric acid, deviations began to appear at higher concentrations. We therefore believe that in the experiments described below we were observing the behavior of primarily monomeric cerium species even though the complexation was strongly dependent upon the composition of the solution.

Results

A. Stoichiometries of Ce(IV) Oxidations. Samples of about 0.1 mmol of various organic acids were treated with 1.0 mmol of Ce(IV) in 50 ml of 0.8 M H_2SO_4, and the solutions were allowed to sit at room temperature 3 to 6 days. Residual Ce(IV) was then determined titrimetrically. The results are presented in Table I.

The stoichiometry observed for bromomalonic acid (BrMA) differs from the 4 equiv reported previously.[5] The difference apparently reflects the longer time before residual cerium(IV) was determined in these subsequent experiments; it can be explained by the observations with formic acid and bromide ion discussed in Results section B below.

B. Oxidation of Formic Acid (FA) and of Bromide Ion. The stoichiometries in Table I indicate that some oxidations stop with formic acid (FA) as a final product while others continue completely to carbon dioxide. Formic acid itself is almost inert to oxidation by cerium(IV) even though the reaction is undoubtedly favored thermodynamically. When 0.02 M Ce(IV) and 0.023 M formic acid are present in 0.8 M H_2SO_4 for 1 to 3 days, the total loss in titer is almost independent of time and corresponds to oxidation of only 1-2% of the formic acid (thesis[2] Table 6).

Bromide ion is slowly oxidized by cerium(IV).[13] When 0.002 M bromide ion and 0.02 M Ce(IV) react in 0.8 M

Table I. Stoichiometries of Oxidation of 0.002 M Organic Acid by 0.02 M Ce(IV) in 0.8 M H_2SO_4

Acid, X		$\Delta[Ce(IV)]/\Delta[X]$
Malonic	MA	5.9
Bromomalonic	BrMA	5.8
Tartronic	TTA	a
Mesoxalic	MOA	4.0^b
Glyoxylic	GOA	1.9
Oxalic	OA	2.0

^{a} Stoichiometries with two different preparations of sodium tartronate were 3.4 and 2.9, and the second preparation gave a very low carbon analysis. Even if TTA is the only M_1 species formed from malonic acid, the stoichiometry could not conceivably be less than 4. A stoichiometry greater than 4 is unlikely because malonic acid itself consumes only 6 equiv, and any value above 4 for TTA would require a corresponding amount of malonic acid be oxidized only to inert GCA. ^{b} The stoichiometry was 3.45 calculated on the assumption the sample was pure sodium mesoxalate. Subsequent elemental analysis indicated a carbon content only 86.5% of theoretical. Correction for this diluent leads to a stoichiometry of 3.99.

H_2SO_4, the loss in titer after 2 days corresponds to complete oxidation to bromine (thesis[2] Table 6). The Ce(IV) titer continues to decrease slowly as an equilibrium mixture of bromine and oxybromine species is approached.

When both 0.002 M bromide ion and 0.023 M formic acid are present with 0.02 M cerium(IV), about a third of the Ce(IV) is reduced in 3 days, and the rate remains fairly constant during that period (thesis[2] Table 6). Thus bromide ion catalyzes the oxidation of formic acid. The probable mechanism is discussed in Discussion section D below.

Three additional experiments involved mixing 0.1 mmol of organic acid with 1.0 mmol of Ce(IV) in 0.8 M H_2SO_4. After 4 days, when the reactions of Table I were complete, 0.1 mmol of Br$^-$ was added to each solution. Much of this ion was presumably oxidized between days 4 and 7, and the change of Ce(IV) titer was then followed between days 7 and 10 (thesis[2] Table 2). Those changes in titer were 0.037 mmol for malonic acid (MA), 0.051 mmol for tartronic acid (TTA), and 0.008 mmol for mesoxalic acid (MOA). These results support the inference from Table I that oxidation of MA or of TTA alone stops while formic acid is still present whereas oxidation of MOA continues to carbon dioxide even if no bromide ion is present. The more complete oxidation of bromomalonic acid (BrMA) presumably takes place because the resulting bromide ion catalyzes slow oxidation of the formic acid that is first formed.

C. Kinetics of Oxidation of Malonic (MA) and Tartronic (TTA) Acids. Solutions about 5 × 10^{-4} M in Ce(IV) were mixed with an excess of an organic species X, and the absorbance was followed spectrophotometrically. For malonic (MA) and tartronic (TTA) acids, the logarithm of absorbance decreased linearly until reaction was nearly complete; these reactions were essentially first order in Ce(IV). The peculiar behavior of bromomalonic acid (BrMA) is discussed further below. Other species reacted too quickly or too slowly for convenient kinetic study.

The spectrophotometric data in any sulfuric or perchloric acid medium could be fitted well to eq 1 suggested by Kasperek and Bruice.[14] Values of these parameters at 25° in 0.8 M H_2SO_4 are presented in Table II.

$$-\frac{d[Ce(IV)]}{dt} = k_{obsd}[Ce(IV)] = \frac{k_2[X][Ce(IV)]}{K_M + [X]} \quad (1)$$

Kasperek and Bruice[14] report k_2 = 0.53 sec^{-1} and K_M = 0.53 M for malonic acid (MA) in 1.5 M H_2SO_4 at 30°. Because our malonic acid concentrations were never as great as 0.01 M, we could not have detected contributions from the K_M term, but our apparent second-order rate constant

Table II. Kinetics of Ce(IV) Consumption in 0.8 M H_2SO_4 at 25°

Acid	k_2, sec^{-1}	K_M, M	k_2/K_M, M^{-1} sec^{-1}
Malonic (MA)		$\gg$[X]	1.04
Tartronic (TTA)	0.0171	0.0060	2.84
Bromomalonic	0.015 (1)	0.107 (1)	0.14 (1)
(BrMA)[a]	0.014 (2)	0.033 (2)	0.42 (2)

[a]Values designated by 1 and 2 in parentheses indicate observations respectively before and after the "break points" discussed in Results section F.

Table III. Activation Energies for Cerium(IV) Oxidations

Acid	Medium	E, kcal/mol
Malonic (MA)	0.8 M H_2SO_4	10.9 ± 0.4
	0.8 M $HClO_4$	6.9 ± 0.1
Tartronic (TTA)	0.8 M H_2SO_4	17.8 ± 0.2
Bromomalonic (BrMA)[a]	0.8 M H_2SO_4	13.0 ± 0.5 (1)
		12.9 ± 0.1 (2)
	0.8 M $HClO_4$	14.6 ± 0.8 (1)
		6.2 ± 0.8 (2)

[a]Values designated 1 and 2 in parentheses indicate observations respectively before and after the "break points" discussed in Results section F.

(thesis[2] Figure 26) is in good agreement with their observations. Kinetics in perchloric acid were not studied in detail.

Oxidation of tartronic acid (TTA) could also be followed spectrophotometrically and fitted to eq 1. The value of k_2 so obtained should be independent of any contamination of TTA by inert material. The K_M value in the table has been corrected from that in the thesis[2] because the stoichiometry for this preparation was 85% of the conceivable minimum even if oxidation stopped cleanly at formic acid. The reaction in perchloric acid was too rapid to follow by procedures available to us.

Activation energies for the reactions of malonic and tartronic acids were calculated from rates at specific concentrations rather than from temperature dependence of the individual rate constants of eq 1. The effects of changing denominator in eq 1 are comparatively small, and the activation energies obtained (thesis[2] Figures 27, 28, 30) are essentially applicable to k_2/K_M. The results are presented in Table III.

D. Rates of Oxidation of Other Nonbrominated Compounds. Mesoxalic (MOA), glyoxylic (GOA), and oxalic (OA) acids are oxidized by cerium(IV) so rapidly that we could not follow the rates conveniently. These species can hardly attain significant concentration during the oxidation of malonic acid or its brominated derivatives.

Glycolic acid (GCA) and formaldehyde are oxidized at less than 1% of the rate of malonic acid (MA). These observations suggest that these species would be end products if they were formed, and the stoichiometry of Table I indicates they are not significant in the reactions of interest. We have not actually done stoichiometric and kinetic measurements to see whether oxidation of these compounds is induced by the oxidation of malonic acid, but the negative results of such experiments with other compounds make it seem doubtful glycolic acid or formaldehyde are intermediates of importance.

We have already discussed (Results section B) the inertness of formic acid (FA) to direct oxidation by its sensitivity to bromide catalyzed oxidation.

E. Oxidation of Mixtures of Nonbrominated Compounds. Mixtures of 0.1 mmol each of two of the three species malonic (MA), tartronic (TTA), and mesoxalic (MOA) acids were treated with 1.5 mmol of Ce(IV) in 0.8 M H_2SO_4. After 5 days, the loss of titer for each of the three possible pairs agreed within 1% with the sum of the values for 0.1
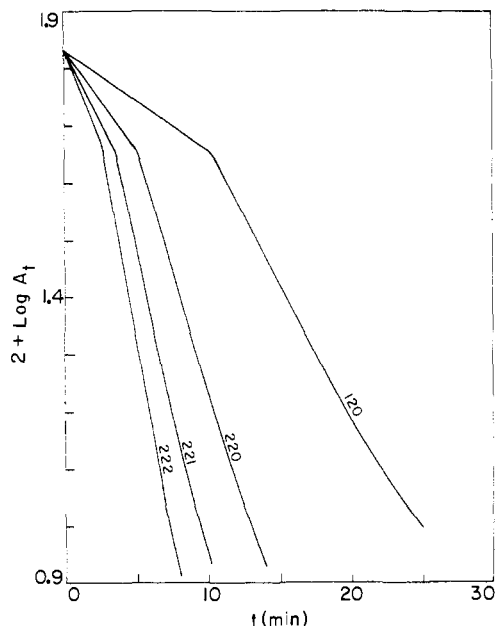
Figure 1. Reaction of Ce(IV) with BrMA in H_2SO_4. For all runs, $[Ce(IV)]_0 = 5.0 \times 10^{-4}$ M and $[H_2SO_4] = 0.8$ M. Values of $[BrMA]_0$ were: 120, 0.005 M; 220, 0.010 M; 221, 0.015 M; 222, 0.020 M. Absorbance (due to Ce(IV) only) was at 390 nm. Temperature was 25°.
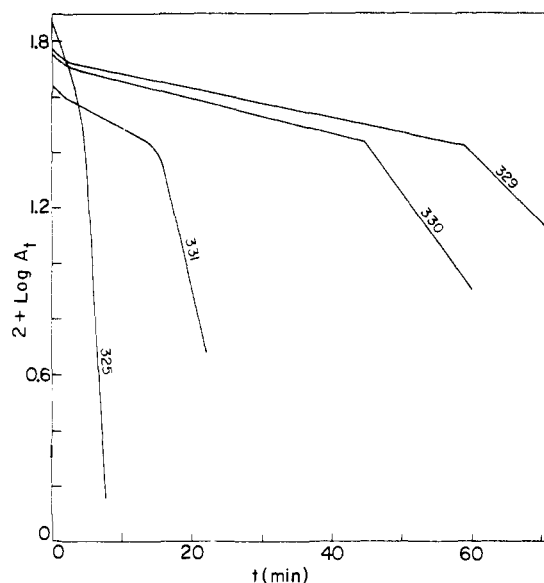
Figure 2. Reaction of Ce(IV) with BrMA in $HClO_4$ + H_2SO_4. For all runs, $[Ce(IV)]_0 = 5.0 \times 10^{-4}$ M, $[BrMA]_0 = 2.5 \times 10^{-3}$ M, and $[HClO_4] = 0.8$ M. Additions of H_2SO_4 were: 325, 0; 331, 0.01 M; 330, 0.05 M; 329, 0.1 M. Run 325 was measured at 320 nm, and the other three runs at 390 nm. Run 325 was at 9°, and the other three were at 10°.

mmol of separate acid (supplementary material[15] Table S1).

The rate of oxidation of a mixture of MA and TTA agreed within 10% with the sum of the rates for the individual species (thesis[2] Table 30).

All of these observations are consistent with the assumption that when no bromide is present then the behavior of the system is what would be expected if the various organic species react independently with cerium(IV).

F. Kinetics of Bromomalonic Acid (BrMA) Oxidation. The reaction of bromomalonic acid (BrMA) with cerium(IV) was followed spectrophotometrically in sulfuric and perchloric media. The peculiar results obtained are illustrated in Figures 1 and 2. There are two different periods

Table IV. Stoichiometry of Bromide Ion Production During Oxidation of 0.01 M BrMA in 0.8 M H_2SO_4 at 25°

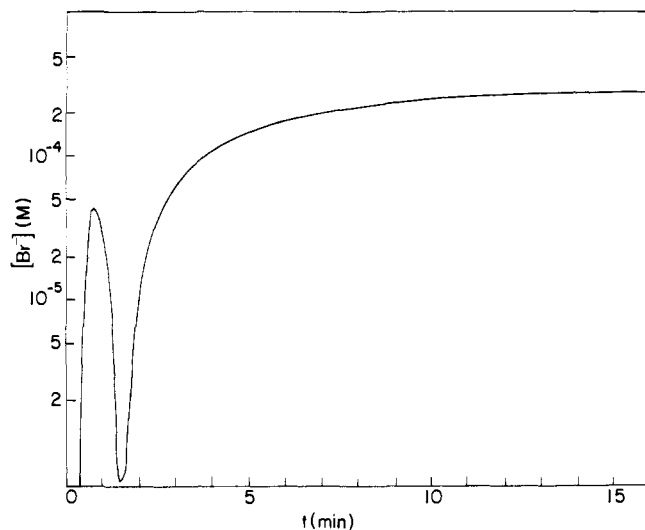| $[Ce(IV)]_0 \times 10^2$, M	$[BrMA]_0/$ $[Ce(IV)]_0$	$[Br^-]_p \times 10^3$, M	$[Ce(IV)]_r/$ $[Br^-]_p$
4.0	0.25	7.3	5.49
3.0	0.33	5.7	5.26
2.0	0.5	3.9	5.13
1.0	1	2.3	4.35
0.5	2	1.4	3.57
0.2	5	0.83	2.27
0.1	10	0.54	1.85
0.05	20	0.38	1.31
0.02	50	0.17	1.18
0.01	100	0.11	0.91

Figure 3. Reaction of Ce(IV) with a mixture of MA + BrMA. Potentiometric trace measures log $[Br^-]$ as 10 ml of Ce(IV) was added dropwise (during about 1 min) to 90 ml of MA + BrMA in H_2SO_4. Immediate mixing would have generated a solution of composition $[Ce(IV)]_0 = 0.005\ M$, $[MA]_0 = 0.020\ M$, $[BrMA]_0 = 0.010\ M$, $[H_2SO_4] = 0.8\ M$. Temperature was 25°.

during which reaction is first order in cerium(IV), and the transition between them is virtually discontinuous. If the two first-order rate constants are designated k_{obsd1} and k_{obsd2}, the ratio k_{obsd2}/k_{obsd1} is usually about 2–3 but is over 7 for run 331 in Figure 2. The ratio becomes smaller as the concentration of sulfuric acid increases, and this fact may explain why Kasperek and Bruice[14] failed to note this remarkable behavior.

The time before the "break point" in the kinetics is approximately inversely proportional to the initial concentrations of BrMA and of Ce(IV), and the total amount of reaction at the break point is approximately independent of those initial concentrations (thesis[2] Table 11). Added sodium bromide (thesis[2] Table 12) and sodium perchlorate (thesis[2] Table 14) have rather little effect on the kinetics. Potassium bisulfate, $KHSO_4$, and sulfuric acid both tend to reduce the rates and to lower the ratio k_{obsd2}/k_{obsd1} (thesis[2] Tables 13 and 14). In perchloric acid medium, increasing acid concentration increases both rates but decreases the ratio k_{obsd2}/k_{obsd1} (thesis[2] Table 16).

Values of k_{obsd1} and k_{obsd2} were fitted to eq 1 (thesis[2] Figure 10) and to the Arrhenius equation (thesis[2] Tables 15 and 18 and Figures 15 and 20). The results are included in Tables II and III.

G. Stoichiometry of Bromide Production from BrMA. Regeneration of bromide ion is a key factor in understanding the mechanism of the Belousov–Zhabotinskii reaction.[5] The stoichiometry of Table I indicates that when cerium(IV) is in excess then 5.8 equiv of oxidant are consumed for each bromide produced by oxidation of BrMA. Data in Table IV show how this ratio decreases as the bromomalonic acid becomes more and more in excess. In this table $[Ce(IV)]_r$ is the concentration of oxidant reacting and $[Br^-]_p$ is the concentration of bromide ion produced. Production of a bromide ion may require as little as 1 equiv of oxidant.

If malonic acid (MA) is also present, the ratio $[Ce(IV)]_r/$ $[Br^-]_p$ is increased. However, the ratio is not even approximately proportional to $[MA]/[BrMA]$ as might be anticipated. Thus an 80-fold excess of MA over BrMA only reduces $[Br^-]_p$ to about a third of the value when the two acids are in equal concentration (thesis[2] Table 5 and Figure 7). The reactions of the two acids do *not* proceed independently of each other.

H. Kinetics of Bromide Production from BrMA. The data in Table IV are stoichiometries when reaction is complete. We have also followed kinetics of bromide ion production. The rates are smooth continuous curves right through conditions under which rates of cerium(IV) consumption change discontinuously! During a typical run, $-d[Ce(IV)]/$ $d[Br^-]$ is about 1.2 initially, falls to a little below unity just before the break point, rises discontinuously to about 2 after the break point, and drops somewhat during the final stages of the reaction (thesis[2] Tables 9–11). Plots of $(d[Br^-]/$ $dt)_0^{-1}$ against $[BrMA]_0^{-1}$ are linear but show small inter-

cepts just as do those designed to evaluate the parameters of eq 1 (thesis[2] Figure 13).

I. Effects of Other Acids on BrMA Reactions. Table V summarizes the effects of adding various other organic species to a reaction mixture consisting initially of 5×10^{-4} M cerium(IV) and 5×10^{-3} M bromomalonic acid (BrMA) in 0.8 M H_2SO_4 at 25°. For malonic (MA) and tartronic (TTA) acids, the rates of cerium consumption are compared with those predicted if the two species were reacting independently.

It is evident the reactions are not independent. Some of the highly reactive adducts were stoichiometrically sufficient to reduce only a small fraction of the cerium(IV) present, yet the accelerated rate of reduction continued for over 3 half-lives of Ce(IV) consumption. The adducts tend to accelerate the initial rate more than the subsequent one and thereby reduce the change of slope at the break point. In fact, 2% of oxalic (OA) or mesoxalic (MOA) acid in the bromomalonic acid (BrMA) can completely eliminate the break point. The accelerating effects on the rate of cerium reduction are in the order OA > MOA > GOA > TTA, MA. In fact, tartronic (TTA) and malonic (MA) acids make contributions that are almost what would be predicted from independent behavior.

If the reactions were independent, small adducts of other acids should have virtually no effect on the initial rate of bromide ion production from bromomalonic acid (BrMA). Table V shows that bromide production is greatly accelerated by most of these adducts. The effect is again in the order OA > MOA > GOA > MA. Tartronic acid (TTA) has little apparent effect on bromide production, and the small apparent rate decrease may be real or may reflect the greater susceptibility of TTA than of BrMA to radical attack.

The above discussion has been based on reactions in 0.8 M H_2SO_4 at 25°. Adducts increase initial rates and thereby tend to eliminate break points. A few experiments were made by adding small amounts of mesoxalic acid (MOA) to the oxidation of BrMA in 0.8 M $HClO_4$ at 10° (thesis[2] Figure 37). These additions reduced the first measurable absorbance indicating immediate consumption of the adduct MOA. Apparent initial rates of Ce(IV) consumption were almost independent of the amount of adduct, but the time

Table V. Effects of Acid Adducts on Rates of Bromomalonic Acid (BrMA) Reactions[a]

Adduct acid, X	$[X]_0 \times 10^5$, M	$k_{obsd1} \times 10^3$, sec^{-1}		$k_{obsd2} \times 10^3$, sec^{-1}		$(d[Br^-]/dt)_0 \times 10^7$, M sec^{-1}
		Obsd	Predicted	Obsd	Predicted	
None		0.68		1.90		2.70
Malonic (MA)	10	1.07	0.78	2.07	2.00	2.78
	20	1.27	0.89	2.11	2.11	3.16
	50	1.63	1.20	2.26	2.42	3.80
	100	2.24	1.72	3.36	2.94	5.10
	500	5.89	5.88	9.15	7.78	7.60
	1000	10.0	11.1	14.8	12.3	9.00
Tartronic (TTA)	5	1.05	0.79	2.22	2.01	2.42
	7	1.07	0.83	2.03	2.05	2.55
Mesoxalic (MOA)	3	1.35		2.18		2.90
	5	2.22		3.07		3.72
	7	4.00		4.00		6.12
Glyoxylic (GOA)	10	1.72		2.78		3.58
	20	2.18		2.87		4.13
	40	3.79		4.62		7.23
Oxalic (OA)	5	2.60		3.80		4.38
	10	5.47		5.47		9.50
	20	15.0		15.0		19.5

[a] Initial conditions were $[Ce(IV)]_0 = 5 \times 10^{-4} M$, $[BrMA]_0 = 5 \times 10^{-3} M$, $[H_2SO_4] = 0.8 M$, temperature 25°.

until the break point was greatly increased by adduct. Therefore, the solution with the largest initial addition of the very reactive MOA and with the largest amount of almost instantaneous reaction actually had the *most* Ce(IV) at the longest times observed! This effect was not investigated in detail, and we have no explanation for it.

J. Bromide Production from MA + BrMA Mixtures. The last column of Table V reports *initial* rates of bromide ion production. The situation with added malonic acid is much more complicated. Figure 3 illustrates the peculiar effect when cerium(IV) is added dropwise to a mixture of malonic (MA) and bromomalonic (BrMA) acids in 0.8 M H_2SO_4. If the cerium(IV) is added all at once, the sharp maximum and subsequent local minimum in [Br$^-$] are real but somewhat less dramatic (thesis[2] Figure 41). Much the same effect is observed if the malonic acid is added 1 min after the other components, but the increase of [Br$^-$] is monotonic if bromomalonic acid is added to a mixture of cerium(IV) and malonic acid that have reacted for 1 min (thesis[2] Figure 40). The bromide ion concentration increases monotonically if the medium is perchloric instead of sulfuric acid (thesis[2] Figure 41).

K. Reactions of Bromide During Malonic Acid Oxidation. Small additions of bromide ion have no effect on behavior of solutions that do not contain malonic acid (MA). Figure 4 illustrates the variation of bromide ion concentration during cerium(IV) oxidation of malonic acid in sulfuric acid medium.

The depletion in bromide ion is accompanied by formation of bromomalonic acid (BrMA). This conclusion was demonstrated by extracting a material that formed bromide by action of Ce(IV), that oxidized iodide ion, and that had a proton NMR spectrum matching that of BrMA.

The initial rate of bromide consumption is approximately proportional to bromide ion concentration and increases with concentrations of Ce(IV) and of MA (thesis[2] Table 31). Of course the change in logarithm of bromide concentration is greatest for the smallest additions of bromide. The peculiar induction periods of about 1 min in Figure 4 are independent of bromide ion concentration but tend to become longer at lower concentrations of Ce(IV) and of MA (thesis[2] Figures 42, 44, 45).

The peculiar break points in cerium(IV) consumption in Figures 1 and 2 accompany smooth curves for bromide production. The induction periods and concentration minima in Figure 4 accompany smooth curves for Ce(IV) consump-
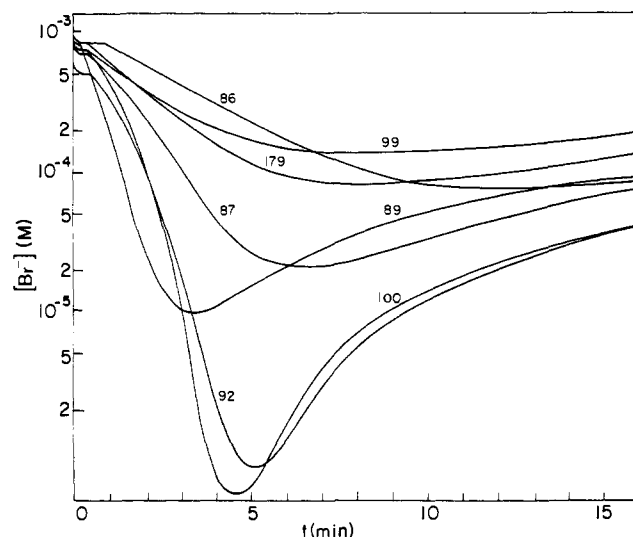
Figure 4. Reaction of Ce(IV) with mixtures of MA + Br$^-$. Potentiometric traces measure log [Br$^-$] at 25° in 0.8 M H_2SO_4. Initial concentrations were (note run 87 is a standard representing intermediate concentrations for all species):

Run	$[Ce(IV)]$, M	$[MA]_0$, M	$[Br^-]_0$
86	0.0050	0.005	0.0010
87	0.0050	0.010	0.0010
89	0.0050	0.020	0.0010
92	0.0050	0.010	0.0008
99	0.0040	0.010	0.0010
100	0.0060	0.010	0.0010
179	0.0050	0.010	0.0012

tion! Addition of bromide ion increases the rate at which Ce(IV) is reduced by malonic acid, the limiting effect being about a factor of 2 (supplementary material[15] Figure S1).

Discussion

A. General Complexities of Mechanism. The material presented above demonstrates that this chemical system is very complex. Most of the molecules in Chart I can form more than one radical during oxidation, and the numerous possible interactions cannot possibly be sorted out completely with the available or attainable information. However, the data do fall into very regular patterns that permit several distinct and previously unanticipated mechanistic

conclusions. We shall attempt to explain the complete mechanism as fully as is justified.

B. Reaction Sequence Based on Stoichiometry. Thermodynamics predict that acidic cerium(IV) can probably oxidize any organic compound to carbon dioxide and water. However, many organic compounds will be inert to such oxidation. The stoichiometries in Table I (Results section A) indicate that malonic acid is oxidized cleanly by the sequence MA → TTA → GOA → FA. Glycolic acid (GCA) and formaldehyde are oxidized so slowly that they would behave as inert products if formed (Results section D); the stoichiometries show they are not formed. We did not actually try to oxidize acetic acid, methane, or methanol, but we have every reason to believe these chemical structures would be inert. Mesoxalic (MOA) and oxalic (OA) acids would be oxidized all the way to carbon dioxide if formed (Table I) in contrast to the stoichiometric evidence that oxidation of malonic acid stops with formic acid.

C. Stoichiometry of BrMA Oxidation. The ultimate stoichiometry of bromomalonic acid oxidation remains ambiguous. A previous[5] observation of 4 equiv suggested the overall process of eq 2. However, bromide ion catalyzed oxidation of the formic acid (Results section B) would increase the total to 6 equiv. Subsequent oxidation of the bromide to elementary bromine would raise it to 7 equiv, and any formation of oxybromine species would push it still higher. The 5.8 equiv reported in Table I must still correspond to an incomplete reaction, and eq 2 is clearly not a description of the total reaction.

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \rightarrow$$
$$Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ \quad (2)$$
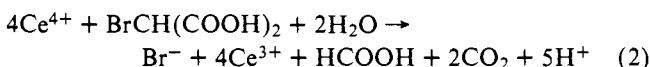
D. Mechanism of Formic Acid Destruction. Formic acid (FA) is inert to the 1-equiv oxidant Ce(IV) (Results section B). However, the C–H bond could be attacked by a 2-equiv oxidant, and both Br_2 and HOBr can accomplish exactly this process.[16] The mechanism of the bromide catalyzed oxidation (Results section B) is probably given by eq 3 and 4. Because we cannot extract significant elementary bromine from a reaction mixture containing formic acid (thesis[2] p 47), eq 3 is probably rate determining for the overall process.

$$2Ce^{4+} + 2Br^- \rightarrow 2Ce^{3+} + Br_2 \quad (3)$$

$$Br_2 + HCOOH \rightarrow 2Br^- + CO_2 + 2H^+ \quad (4)$$
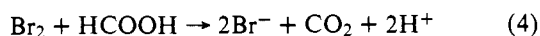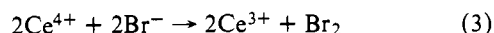
E. Mechanism of Initial Ce(IV) Attack. Even though cerium(IV) is thermodynamically capable of oxidizing all of these organic species, the rates of reaction differ enormously. Mesoxalic (MOA), glyoxylic (GOA), and oxalic (OA) acids are all destroyed within a minute or two. Each has a carbonyl group adjacent to a carboxyl and can form a five-member chelate ring like structure I. In this structure, Y

I
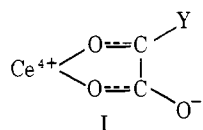
may be H(GOA), O⁻(OA), or CO_2^-(MOA). The C–C bond in the ring almost certainly breaks during the process that initiates oxidation of oxalic acid (OA), and the same step may initiate oxidation of the other species in this group. However, the argument developed in Discussion section L below seems to imply that GOA is at least sometimes oxidized to a radical that can regenerate GOA by reaction with other molecules; such a conclusion requires that the C–H bond rather than the C–C bond be broken in the initial oxidation to a radical.

Malonic (MA), bromomalonic (BrMA), and tartronic (TTA) acids react more slowly but still reduce any available cerium(IV) within a few minutes. Each has two carboxyl groups and can form a six-member chelate ring like structure II. In this structure, Z may be H(MA),

II
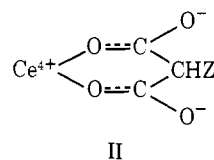
OH(TTA), or Br(BrMA). For oxidation to occur, the CHZ group may lose a proton to solvent, and the central cerium ion may accept an electron.

The other compounds in Chart I have neither two carboxyl groups nor a carbonyl adjacent to a carboxyl, and they all react so slowly with cerium(IV) that they may be considered inert for purposes of this discussion.

F. Hydrolysis of Bromomalonyl Radical. One of the remarkable discoveries reported here is the great stoichiometric efficiency with which cerium(IV) can generate bromide ion from bromomalonic acid (BrMA). Although the stoichiometry in Table I indicates at least 5.8 equiv of Ce(IV) are ultimately consumed for each bromide ion produced, initial rates require little more than 1 equiv per bromide (Results section H and Table IV). The very first Ce(IV) attack must have the effect of liberating a bromide ion to solution. The fragment formed by the oxidation itself could hardly be negative like Br⁻, and we propose that the oxidative decomposition of structure II leads to a proton and a bromomalonyl radical. The negative bromide ion is proposed to come from the almost instantaneous hydrolysis of the radical by eq 5.

$$BrC(COOH)_2 + H_2O \rightarrow HOC(COOH)_2 + Br^- + H^+ \quad (5)$$
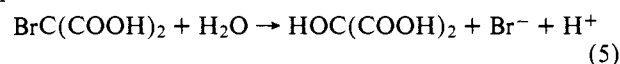
G. Oxidative Bromination of Malonyl Radicals. During periods of only a few minutes, bromide ion has very little effect on any of the rates studied here *unless* malonic acid (MA) is present. However, simultaneous presence of Ce(IV) + MA + Br⁻ results in formation of bromomalonic acid (Results section K). The reaction is too rapid to occur by oxidation of bromide[13] and subsequent bromination of malonic acid. The observations apparently require oxidative bromination of malonyl radical by the net process of eq 6. The mechanism presumably involves either a $CeBr^{3+}$ complex reacting with a radical or a malonyl complex of cerium(IV) reacting with a bromide ion, and electron transfer accompanies formation of the C–Br bond.

$$Ce^{4+} + Br^- + H\dot{C}(COOH)_2 \rightarrow Ce^{3+} + BrCH(COOH)_2 \quad (6)$$
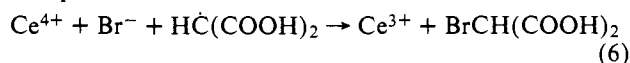
H. Oxidation vs. Disproportionation of Radicals. A molecule from Chart I is oxidized to a radical by the generalized process of eq 7. The subsequent fate of the radical may involve either oxidation by cerium(IV) (eq 8) or disproportionation with another radical (eq 9). Both processes are well precedented and undoubtedly occur. Both result in the same stoichiometry that 2 equiv of Ce(IV) are consumed for each mole of M_{n+1} produced. However, two independent pieces of evidence indicate that at least some of the radicals of this study are more likely to disproportionate (eq 9) than to be directly oxidized.

$$Ce^{4+} + M_n \rightarrow Ce^{3+} + R_{n\cdot} + H^+ \quad (7)$$

$$Ce^{4+} + R_{n\cdot} + H_2O \rightarrow Ce^{3+} + M_{n+1} + H^+ \quad (8)$$

$$2R_{n\cdot} + H_2O \rightarrow M_n + M_{n+1} \quad (9)$$

1. Bromide ion has little effect on the rate of oxidation of any species except malonic acid (MA), but with this species, the rate of cerium(IV) consumption can be increased by a factor of up to 2 (Results section K). It is very doubtful that bromide increases the rate of primary Ce(IV) attack on malonic acid and on no other molecule. Rather, step 6 is stoichiometrically equivalent to step 8 and could double the rate of cerium(IV) consumption if step 9 is dominant in the absence of bromide ion.

2. During the oxidation of bromomalonic acid (BrMA), the initial value of $-d[Ce(IV)]/d[Br^-]$ is often as low as about 1.2 (thesis[2] Table 9). If the hydrolyzed radicals from step 5 are oxidized by step 8, the value would be 2 to 4 depending upon the extent to which the resulting glyoxylic acid (GOA) further reacted. The value only a little greater than unity indicates that step 9 is the predominant one for these radicals.

The above arguments are not absolutely unequivocal and do not necessarily apply to all possible radicals in the system. However, cerium(IV) apparently oxidizes molecules by first forming bidentate complexes that subsequently undergo electron rearrangement. Radicals at very low concentration would not compete well with molecules for forming complexes, and it is not necessarily surprising that facile radical–radical reactions compete well with oxidations.

I. Decarboxylation of Three-Carbon Species. The M_0 molecule malonic acid (MA) contains three carbon atoms. The argument of Discussion section B indicates that all three atoms are retained during oxidation to the M_1 molecule tartronic acid (TTA) but that one carbon is lost quantitatively as carbon dioxide during oxidation to the M_2 molecule glyoxylic acid (GOA). We must also recognize the argument of Discussion section H that much of the M_2 product is formed by a radical–radical disproportionation reaction rather than by a cerium(IV) oxidation.

The malonyl radical must retain all three carbons during the processes that convert it to tartronic acid (TTA). The hydroxymalonyl radical, $HO\dot{C}(COOH)_2$, could conceivably undergo acid catalyzed tautomerization and radical decarboxylation to $HO\dot{C}HCOOH$, but such a radical would undoubtedly generate glycolic acid (GCA) in some of its subsequent reactions; radical decarboxylation apparently does not occur.

On the other hand, hydroxymalonyl radical disproportionation would be expected to form mesoxalic acid (MOA) as one of the products, and this reaction also does not occur.

We can escape this dilemma only by proposing that the hydroxymalonyl radical rapidly tautomerizes to form another (tartronyl) radical which can disproportionate only by abstracting a carboxyl hydrogen. The proposed sequence is eq 10 and 11.

$$HO\dot{C}(COOH)_2 \xrightarrow{H^+} \cdot OCH(COOH)_2 \qquad (10)$$

$$2 \cdot OCH(COOH)_2 \rightarrow$$
$$\underset{(TTA)}{HOCH(COOH)_2} + \underset{(GOA)}{O{=}CHCOOH} + CO_2 \quad (11)$$

J. Radical Attack on MA. Discussion section H discussed the alternatives that radicals might react either with cerium(IV) or with other radicals. They might also react with other organic molecules by hydrogen abstraction. The intermediate molecules that form during the oxidation of malonic acid react with cerium(IV) more rapidly than does malonic acid itself. If those radicals abstracted hydrogen from malonic acid, the oxidation reaction would be autocatalytic.

Actually, the oxidation of malonic acid exhibits remarkably clean kinetics. The apparent first-order rate constant

for Ce(IV) consumption does tend to drift up slightly as an individual run progresses, but the effect is never more than about 30% (thesis[2] Table 19). Although the overall process requires 6 equiv of oxidant, the effective rate-determining step is obviously eq 12. Radicals derived from partially oxidized species do not attack malonic acid significantly.

$$Ce^{4+} + CH_2(COOH)_2 \rightarrow Ce^{3+} + \cdot CH(COOH)_2 + H^+$$
$$(12)$$

The argument can even be turned around to show that malonyl radicals do attack tartronic acid (TTA). The data in Table II show that tartronic acid is only two to three times as reactive with cerium(IV) as is malonic acid itself. If the intermediate tartronic acid were destroyed only by reaction with Ce(IV), the kinetic behavior during an individual run would be nowhere nearly as clean as we observe.[17] We conclude that during the oxidation of malonic acid destruction of much of the intermediate tartronic acid is initiated not by cerium(IV) oxidation but by eq 13.

$$HOCH(COOH)_2 + \cdot CH(COOH)_2 \rightarrow$$
$$\cdot OCH(COOH)_2 + CH_2(COOH)_2 \quad (13)$$

K. Radical Attack on BrMA. As discussed in Discussion section J, the C–H bond in malonic acid is sufficiently strong that malonic acid is virtually inert to attack by other organic radicals while malonyl radical can abstract hydrogen from many of the intermediate molecules formed during oxidation.

Bromomalonic acid (BrMA) is not similarly inert to attack. Except for tartronic acid (TTA), all of the species that we tested could greatly increase the rate at which bromide ion was liberated during oxidation of BrMA (Results section I and Table V). Even 1% of adduct acid in BrMA could sometimes double the rate of bromide production. The stoichiometric observations on mixtures of MA and BrMA (thesis[2] Table 5 and Figure 7) also indicate that malonyl radicals attack BrMA with liberation of bromide ion.

We conclude that various intermediate radicals are very effective at attacking bromomalonic acid to form bromomalonyl radicals which then hydrolyze by step 5. This fact has important implications for the mechanism of the Belousov–Zhabotinskii reaction.[18]

L. Break Points during BrMA Oxidation. Probably our most dramatic and unexpected observations are associated with the almost discontinuous "break points" illustrated in Figures 1 and 2. Although the rate of consumption of a reagent may increase as the concentration of a reactive intermediate builds up, such a consecutive process could not generate the discontinuous changes we observe.[17]

We are also unable to model these abrupt changes if we add a postulate that an intermediate species also affects the rate by preferential complexing with the small amount of cerium(IV) present.

We can explain our observations if we propose the same sort of "switching" mechanism that describes the behavior of bromous acid in the Belousov–Zhabotinskii reaction.[5,6] If a stoichiometrically insignificant species[19] is formed by processes that are zero and first order in its concentration and is destroyed by processes that are first and second order, its concentration will switch almost discontinuously between two different steady states whenever the effect of the first-order terms changes between net formation and net destruction.[6]

A skeleton mechanism consistent with the above arguments starts with eq 14, which includes the net consequences of eq 5 and 10 in addition to the initial oxidative at-

tack on BrMA. If eq 11 is added, the overall effect is that of eq 15.

$$BrMA + Ce(IV) \rightarrow Br^- + Ce(III) + R_1\cdot \qquad (14)$$

$$2BrMA + 2Ce(IV) \rightarrow 2Br^- + TTA + GOA + 2Ce(III) \qquad (15)$$

The resulting glyoxylic acid reacts almost as rapidly as formed (Results section D) by eq 16.
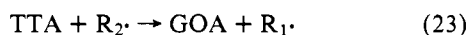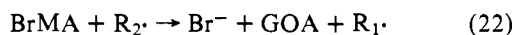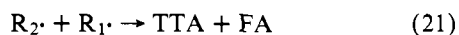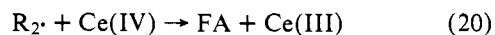
$$GOA + Ce(IV) \rightarrow R_2\cdot + Ce(III) \qquad (16)$$

The concentration of $R_2\cdot$ radicals is always low and can be described by steady state eq 17 and 18. In these equations α and γ must be positive while β may have either sign. The α term is one-half[20] the rate of eq 14. The $\gamma[R_2\cdot]^2$ term is equal[20] to the rate of eq 19.

$$d[R_2\cdot]/dt = \alpha + \beta[R_2\cdot] - \gamma[R_2\cdot]^2 = 0 \qquad (17)$$

$$[R_2\cdot] = (\beta + \sqrt{\beta^2 + 4\alpha\gamma})/2\gamma \qquad (18)$$

$$2R_2\cdot \rightarrow GOA + FA \qquad (19)$$

Negative contributions to the $\beta[R_2\cdot]$ term are provided by the rates[20] of eq 20 and 21. Positive contributions are half[20] the rates of eq 22 and 23 when followed by eq 11 and 16.

$$R_2\cdot + Ce(IV) \rightarrow FA + Ce(III) \qquad (20)$$

$$R_2\cdot + R_1\cdot \rightarrow TTA + FA \qquad (21)$$

$$BrMA + R_2\cdot \rightarrow Br^- + GOA + R_1\cdot \qquad (22)$$

$$TTA + R_2\cdot \rightarrow GOA + R_1\cdot \qquad (23)$$

At the start of a reaction when [Ce(IV)] is large and [TTA] is small, β will be negative and $[R_2\cdot]$ can be approximated by $-\alpha/\beta$. As reaction proceeds, these concentrations will shift until β becomes positive. At that time, $[R_2\cdot]$ will change almost discontinuously to β/γ and the rate of consumption of Ce(IV) will jump dramatically. If eq 23 is more important than eq 22, the rate of bromide production will not change significantly when the concentrations of GOA and R_2 and the rate of Ce(IV) consumption change almost discontinuously (Results sections F–H).

The above mechanism appears to be consistent with the observations except that it cannot explain a value of $-d[Ce(IV)]/d[Br^-]$ much below 2. We can accommodate this feature by adding plausible eq 24 which is the net result of a sequence that includes eq 5 and 10. This reaction is also necessary to explain the number below unity for the last entry in Table IV.

$$R_1\cdot + BrMA + H_2O \rightarrow Br^- + TTA + R_1\cdot \qquad (24)$$
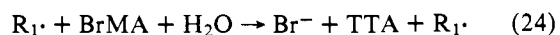
M. Maxima and Minima in Bromide Concentration. Another very peculiar feature of our observations involves the maxima and minima in bromide concentration when malonic acid and cerium(IV) react in the presence of either bromide ion or bromomalonic acid (BrMA) (Figures 3 and 4).

When Ce(IV) is added to BrMA, production of Br^- starts immediately and proceeds as a smooth curve without any suggestions of the break points observed after a few minutes for Ce(IV) consumption in the same system (thesis[2] Figures 12 and 18). When Ce(IV) is added to MA + BrMA, production of Br^- also starts immediately and continues for about 1 min before $[Br^-]$ reaches a sharp maximum and decreases rapidly (Figure 3). When Ce(IV) is allowed to react with the MA for 1 min before the BrMA is added, the maximum does not occur (thesis[2] Figure 40). When Ce(IV) is added to MA + Br^-, $[Br^-]$ decreases

slightly during the first few seconds presumably due to complexing to species like $CeBr^{3+}$; $[Br^-]$ then remains unchanged for about 1 min before it discontinuously begins to decrease.

The decrease in $[Br^-]$ in the systems containing MA is almost certainly due to formation of BrMA by reaction of malonyl radicals with Ce(IV) + Br^- (Discussion section G). The break points after about 1 min in Figures 3 and 4 and the absence of a $[Br^-]$ maximum if addition of BrMA is delayed indicate that some intermediate must be formed before BrMA synthesis is possible. We cannot speculate fruitfully except to note that the K_M values in Table IV indicate that TTA complexes Ce(IV) much more strongly than either BrMA or MA and can conceivably change behavior of the system at concentrations which are low but comparable to [Ce(IV)].

As Figures 3 and 4 illustrate, $[Br^-]$ goes through a minimum after a few minutes in both the Ce(IV) + MA + BrMA and Ce(IV) + MA + Br^- systems. Either BrMA synthesis (which consumes Br^-) is more than first order in Ce(IV), or two intermediate species such as TTA and GOA affect BrMA synthesis and Br^- liberation from BrMA differently. No further comments appear justified at present.

N. Concluding Remarks. Study of this complicated system was initiated because the processes were associated with a very efficient chemical oscillator. The implications for that system are discussed briefly in a subsequent paper.[18] As the work progressed, many unusual but highly reproducible kinetic features were observed. These features greatly limited the mechanistic possibilities, and we have used this system as something of a test and example of how far it is possible to go in elucidating a complicated chemical system.

The ultimate objective of mechanistic chemistry must be the identification and kinetic characterization of all of the elementary processes that combine to produce total chemical change. The necessary accumulation of information (and the retrieval for application to other related systems!) presents major problems that are only dimly foreseen. However, the problems are beginning to be recognized and chemical understanding is continuing to develop.

Supplementary Material Available. As has been indicated during the discussion, the detailed evidence on which the arguments are based is available in Dr. Jwo's thesis.[2] Table S1 and Figure S1 dealing with material obtained subsequent to that thesis will appear immediately following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5422.

References and Notes

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Oscillations in Chemical Systems. X.[1] Implications of Cerium Oxidation Mechanisms for the Belousov–Zhabotinskii Reaction

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Abstract: Although oxidations of malonic acid derivatives by cerium(IV) involve very complicated mechanisms, the mixture of unoxidized and partially oxidized species in an oscillating solution will react by kinetics first order in Ce(IV). The apparent rate constant will be such that oscillations may occur only if between 0.25 and 0.75 bromide ions are produced per cerium(IV) ion consumed. The stoichiometry originally proposed does not quite fall in this range, but addition of hypobromous acid oxidation of formic acid generates exactly the stoichiometry of maximum sensitivity to oscillation. Explanation of oscillations also requires that malonyl radicals preferentially attack bromomalonic acid to liberate bromide ions. We have not been able to resolve complications involving possible independent oxidation of malonic acid, possible accumulation of tartronic acid, and possible oxidation of organic molecules by oxybromine intermediates, but we do not believe these complications are serious.

Chemical oscillators must be considered among the most complicated of chemical systems. Probably the best characterized homogeneous oscillator is the Belousov–Zhabotinskii reaction[2,3] involving the cerium ion catalyzed oxidation of malonic acid by acidic bromate. The principal features of the mechanism are now well established.[4,5]

An important component of this mechanism is the oxidation of a mixture of malonic (MA) and bromomalonic (BrMA) acids with liberation of bromide ion. The previous paper[1] has elucidated many features of the sequence of events by which this oxidation occurs. The reaction is unexpectedly complex, and the observations include sudden virtually discontinuous changes in rate. It is the object of the present paper to show that these mechanistic complications of the oxidation reaction are probably of very little significance to the understanding of the oscillating Belousov–Zhabotinskii reaction!

Pertinent Experimental Facts

The Belousov–Zhabotinskii reaction involves repeated oscillation in the oxidation state of the system. These oscillations can be followed by observing the [Ce(IV)]/[Ce(III)] ratio directly or by using a redox indicator such as ferrous phenanthroline. The concentration of bromide ion undergoes synchronous oscillations that can be followed potentiometrically with an ion specific electrode. Relative concentrations of reactants can greatly affect the period, amplitude, and shape of these oscillations. We restrict comment here to three chemical observations of significance to the subsequent discussion.

1. Thermodynamic data demonstrate that in an acidic bromate, BrO_3^-, solution elementary bromine, Br_2, is the only other inorganic bromide species that can be present in stoichiometrically significant concentration (ref 4, pp 8652 and 8653). Elementary bromine reacts rapidly and irreversibly with malonic acid. Therefore, virtually all of the bromine in a Belousov–Zhabotinskii system is present either as bromate or in organic combination.

2. Studies by Hess et al.[6,7] indicated that about 75% of the organically bound bromine is present as monobromomalonic acid (BrMA), and the remainder as dibromoacetic acid, $Br_2CHCOOH$. No other bromine-containing compounds were detected. Somewhat similar studies in this laboratory (ref 4, p 8652) indicated 85–95% of organic bromine as BrMA and the remainder as monobromoacetic acid. The apparent discrepancies undoubtedly reflect different extents of bromination of malonic acid and different times before analysis of the two test solutions; the two studies agree that the major part of the organically bound bromine is present as BrMA.

3. Stoichiometry of the Ce(IV) oxidation of malonic acid (MA) indicates 1 mol of formic acid (FA) product for each mole of reductant (ref 1, Results section A). However, Hess et al.[8] were unable to detect any formic acid in a solution that had undergone repeated oscillations. Failure to detect this material indicates that reactions with cerium(IV) alone are not enough to explain all behavior of organic species in the Belousov–Zhabotinskii reaction.

Basic Chemical Mechanism

The essential features of the chemical mechanism[4] are summarized in steps C1 to C5. Steps C1 and C2 lead to reduction of bromate by bromide ion; the reactant species retain paired electrons at all times. Steps C3 and C4 lead to reduction of bromate by cerium(III). The mechanism assumes step C3a is rate determining for the autocatalytic generation of bromous acid, but this species does not attain massive concentrations because of the second-order destruc-