(Nujol) 1730, 1665 (w), 1320, 1245, 1170, 1145, 1103, 1072, 1013, 968, 923, 912, 880, 857, 834, 805, 770, 735 cm^{-1}.

Phosphoramidite 5 (2.00 g, 9.44 mmol) and **2** (0.66 g, 4.7 mmol) for 350 hr at 120° showed 80% conversion of **2** to **11** (65% yield by vpc) isolated by distillation as a viscous, colorless liquid (0.40 g, 1.1 mmol), 30%, bp 95–100° (0.1 Torr). A considerable amount of polymer **12** precipitated from solution during reaction but was not quantitatively measured. **11** reacted rapidly on warming with sulfur to give the thio compound **11s**, a pale yellow liquid isolated by preparative vpc.

Phosphoramidite 6 (11.6 g, 71.4 mmol) and **2** (5.00 g, 35.7 mmol) gave complete conversion of **2** to products in 19 hr at 115° yielding 60% of **10** (by vpc) and several minor unidentified products. A large amount of **12** also was formed. Distillation yielded pure **10**, a colorless viscous liquid, 4.0 g, 13 mmol (37%), bp 87–88° (0.06 Torr). Reaction of **10** with sulfur gave a solid which was recrystallized several times from hexane, mp 93.5–94°. With excess methyl iodide, **10** formed the methyl phosphonium salt, a white solid, which was washed several times with pentane to give a white solid: mp 175–177°; pmr (CDCl$_3$) δ 1.38 (6 H, s, gem CH$_3$), 1.64 (3 H, d, J_{HP} = 3.5 Hz, vinyl CH$_3$), 1.80 (3 H, d, J_{HP} = 2.5 Hz, vinyl CH$_3$), 2.45 (3 H, d, J_{HP} = 15 Hz, PCH$_3$), 2.98 (6 H, d, J_{HP} = 11 Hz, PN(CH$_3$)$_2$), 2.94 (6 H, s, CON(CH$_3$)$_2$); ir (Nujol) 1665, 1620 (w), 1315, 1255, 1175, 1111, 1095, 1059, 1011, 975, 950, 926, 910, 877, 859, 806, 734, 672 cm^{-1}.

Anal. Calcd for $C_{15}H_{33}N_3O_2PI$: C, 40.45; H, 7.47. Found: C, 40.54; H, 7.35.

Registry No.—**1,** 933-52-8; **2,** 3173-79-3; **3,** 20217-54-3; **4,** 17166-16-4; **5,** 26546-75-8; **6,** 1608-26-0; **7,** 20217-34-9; **7s,** 32687-54-0; **8,** 20217-52-1; **8** MeI, 32654-72-1; **8s,** 32687-56-2; **10,** 20217-33-8; **10** MeI, 32687-58-4; **10s,** 32687-24-4; **11,** 32687-25-5; **11s,** 32687-26-6; **13,** 32654-70-9; **15,** 32687-27-7; **16,** 32687-28-8.

Kinetic Analysis of Silver-Catalyzed Oxidative Cleavage Reactions by Peroxydisulfate Ions[1]

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The rates of the silver(I)-catalyzed oxidative cleavage reactions of pinacol (**1**), 2-methyl-2-hydroxy-3-butanone (**2**), and pyruvic acid (**3**) by potassium peroxydisulfate have been measured at various concentrations of the reactants. The observed rates indicate that two reaction paths are operative in these cleavage reactions. In path I, the oxidative cleavage is performed by silver(III). Path II is a free-radical chain reaction that involves silver(II) as the oxidative cleaving agent. Oxidative cleavage by path II is faster than path I and predominates at lower substrate concentrations, whereas the slower path I is more likely if the substrate concentration is high or if the substrate reacts rapidly with silver(III).

The silver(I)-catalyzed oxidative cleavage reactions of glycols by peroxydisulfate was demonstrated by Greenspan and Woodburn.[2] Kinetic studies of the cleavage reactions of α-hydroxy acids and esters show that the rate laws for the cleavage reactions are dependent on the concentrations of the reagents and, in some instances, the reaction rates are inversely related to the substrate concentration.[3-8] Our investigations were directed toward finding an explanation for the kinetic behavior of these oxidative cleavage reactions. A mechanistic rationale for the kinetics of the oxidative cleavage reactions of pinacol (**1**), 2-methyl-2-hydroxy-3-butanone (**2**), and pyruvic acid (**3**) yielding the products shown in eq 1, 2, and 3, respectively (see Experimental Section), is presented in this article.

$$\underset{\mathbf{1}}{(CH_3)_2C(OH)C(OH)(CH_3)_2} + S_2O_8^{2-} \xrightarrow{Ag^I} 2(CH_3)_2C{=}O + 2HSO_4^- \tag{1}$$

$$\underset{\mathbf{2}}{(CH_3)_2C(OH)COCH_3} + S_2O_8^{2-} \xrightarrow{Ag^I} (CH_3)_2C{=}O + CH_3CO_2H + 2HSO_4^- \tag{2}$$

$$\underset{\mathbf{3}}{CH_3COCO_2H} + S_2O_8^{2-} \xrightarrow{Ag^I} CH_3CO_2H + CO_2 + HSO_4^- \tag{3}$$

Kinetic Data.[3]—In the absence of Ag^I, the rate of reaction of the peroxydisulfate with compounds **1**, **2**, and **3** at 30° in a sulfate–bisulfate buffered solution (pH 1.4) is negligible. Upon addition of Ag^I, immediate reaction ensues. Preliminary studies by us, as well as the previously cited investigations by others,[3-8] showed that the rate laws for the reactions depended markedly on the relative concentrations of the reagents. Initial rates for the oxidative cleavage reactions of **1**, **2**, and **3** at various initial concentrations of Ag^I, the substrate, and peroxydisulfate are shown in Tables I, II, and III, respectively.

Examination of the oxidative–cleavage rates for pinacol in Table I reveal the following. (1) At the higher [Ag^I] and pinacol concentrations, the cleavage rates are essentially zero order in substrate and first order in Ag^I. (2) At the higher [Ag^I] but lower substrate concentrations, the reaction rates are half-order in both Ag^I and the substrate. (3) At the lowest [$S_2O_8^{2-}$], the reaction rates are zero order in pinacol and half order in [Ag^I]. (4) At low [Ag^I] but higher ($S_2O_8^{2-}$] and pinacol concentrations, the reaction rates are zero order in substrate but approach three-halves order in [Ag^I]. (5) The kinetic order of $S_2O_8^{2-}$ is considerably greater than unity except at low substrate concentrations. (6) At low [Ag^I], the reaction rate appears to be inversely related to the pinacol concentration.

The oxidative cleavage rates of the hydroxy ketone **2** and pyruvic acid (**3**) show some of the characteristics observed for the pinacol reaction. The most significant difference is that the inverse concentration effect

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[1] This work was supported by a grant (AM-08517) from the National Institutes of Health.

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[3] D. D. Mishra and S. Ghosh, *J. Indian Chem. Soc.*, **41**, 397 (1964).

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TABLE I

INITIAL RATES[a] OF OXIDATIVE CLEAVAGE OF PINACOL (1) AT 30.0° [b]

$[S_2O_8^{2-}]$ × 10²	$[Ag^I]$ × 10³	[Pinacol] 0.30	0.15	0.075	0.018	0.0094
4.0	5.12	37.95	37.50	36.92		8.70
1.0	5.12	4.48	4.41	4.43	2.16	1.54
0.5	5.12	0.87	0.86	0.86		0.82
4.0	2.56	18.82	20.38	22.43		5.09
1.0	2.56	2.49	2.48	2.77	1.38	1.01
0.5	2.56	0.52	0.52	0.53		0.47
4.0	1.28	5.34	8.65	10.74		2.27
1.0	1.28	1.27	1.28	1.31		0.64
0.5	1.28	0.38	0.38	0.39		0.33
1.0	0.64	0.37	0.46	0.45	0.51	0.37
1.0	0.32	0.12	0.15	0.36	0.20	0.27

[a] All rates estimated from first 10% reaction of $S_2O_8^{2-}$ and are expressed in mol l.$^{-1}$ min^{-1} × 10⁴. [b] Solutions buffered at pH 1.4 by 0.25 *M* Na_2SO_4 and 0.25 *M* $NaHSO_4$.

TABLE II

INITIAL RATES[a] OF OXIDATIVE CLEAVAGE OF 2-METHYL-2-HYDROXY-3-BUTANONE (**2**) AT 30.0° [b]

$[S_2O_8^{2-}]$ × 10²	$[Ag^I]$ × 10³	[**2**] 0.30	0.15	0.075	0.0187	0.0094
1.0	5.12	0.99	1.08	1.09	0.91	0.066
4.0	2.56	2.97		4.23		2.13
1.0	2.56	0.51		0.54		0.43
0.5	2.56	0.15		0.26		0.21
1.0	1.28	0.26	0.37	0.39	0.37	0.34
4.0	0.64	0.79		2.19		0.89
1.0	0.64	0.095		0.24	0.16	0.11
0.5	0.64	0.036		0.057		0.031

[a] All rates estimated from first 10% reaction of $S_2O_8^{2-}$ and are expressed in mol l.$^{-1}$ min^{-1} × 10⁴. [b] Solutions buffered at pH 1.4 by 0.25 *M* Na_2SO_4 and 0.25 *M* $NaHSO_4$.

TABLE III

INITIAL RATES[a] OF OXIDATIVE CLEAVAGE OF PYRUVIC ACID (**3**) AT 30.0° [b]

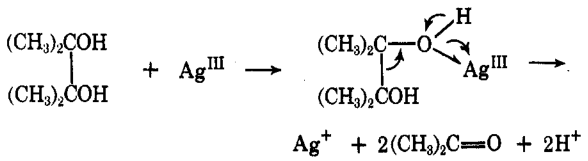
$[S_2O_8^{2-}]$ × 10²	$[Ag^I]$ × 10³	[Pyruvic acid] 0.075	0.0188	0.0094	0.0047
1.0	5.12	0.35	0.51	0.62	0.99
4.0	2.56	1.30	3.14		5.65
1.0	2.56	0.20	0.39		0.76
0.5	2.56	0.17	0.17		0.26
1.0	1.28	0.18	0.26	0.35	0.57
4.0	0.64	0.64	1.02		2.74
1.0	0.64	0.088	0.12		0.39
0.5	0.64	0.026	0.042		0.10

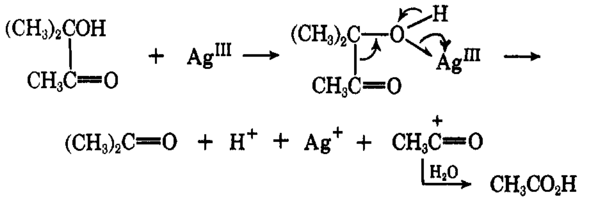
[a] All rates estimated from first 10% reaction of $S_2O_8^{2-}$ and are expressed in mol l.$^{-1}$ min^{-1} × 10⁴. [b] Solutions buffered at pH 1.4 by 0.25 *M* Na_2SO_4 and 0.25 *M* $NaHSO_4$.

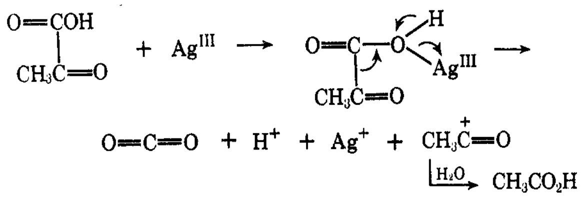
of the substrate on the reaction rates (item 6 above) is more pronounced and operative even at higher $[Ag^I]$.

These kinetic observations can be rationalized in terms of two paths for the oxidative–cleavage reactions. In path I, the cleavage is effected by Ag^{III} which is formed by oxidation of Ag^I by $S_2O_8^{2-}$.(9) Path II is a free-radical chain reaction involving Ag^{II} as the oxidative cleaving agent in a free-radical chain propagating process.

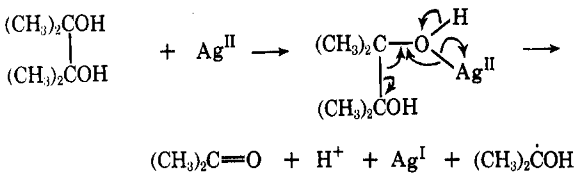
Path I.—Oxidative cleavage of the substrates **1**, **2**, and **3** may be performed by Ag^{III} as shown in eq 4, 5, and 6.(10) The acylium ion formed in the cleavage reaction of the hydroxy ketone **2** and pyruvic acid (**3**) reacts with water producing the acetic acid observed as a reaction product in each case.


(4)


(5)


(6)

Path II.—In path II, the cleavage is performed by Ag^{II} as part of a free-radical chain reaction. In the case of pinacol, the cleavage by Ag^{II} produces an α-hydroxyalkyl radical which reacts with $S_2O_8^{2-}$ yielding another molecule of acetone and a chain propagating $SO_4\cdot^-$. Oxidation of Ag^I by $SO_4\cdot^-$ regenerates Ag^{II} (reaction 9) for the oxidative cleavage reaction. Oxidative cleavage of the hydroxy ketone **2** and pyruvic acid in path II follows similar routes. An acetyl radical is formed in the cleavage reactions of **2** and **3** which propagates the chain by interaction with $S_2O_8^{2-}$ yielding both the chain carrying $SO_4\cdot^-$ and the acylium cation, the precursor of acetic acid. Both α-hydroxyalkyl radicals and acyl radicals have been proposed to react with peroxydisulfate(11) yielding the sulfate anion radical necessary to propagate the chain reaction by interaction with Ag^I as shown in eq 9.


(7)

$$(CH_3)_2\dot{C}OH + S_2O_8^{2-} \longrightarrow (CH_3)_2C{=}O + H^+ + SO_4^{2-} + SO_4^{\cdot-} \quad (8)$$

$$SO_4^{\cdot-} + Ag^I \longrightarrow SO_4^{2-} + Ag^{II} \quad (9)$$

Kinetic Analysis.—Support for these proposed mechanisms for the oxidative cleavage reactions is found in

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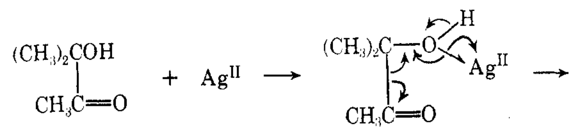
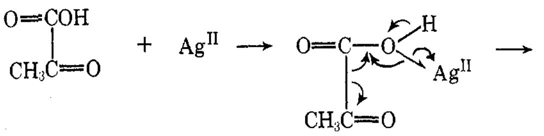
(9) For reviews of the chemistry of the higher oxidation states of silver, see J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962); D. A. House, *ibid.*, **62**, 185 (1962).

(10) Although both Ag^{III} and Ag^{II} are able to form dsp²-square-planar complexes with substrates capable of undergoing oxidative cleavage, our investigations of the oxidative cleavage rates of stereoisomeric cyclic 1,2 diols to be reported later indicate that formation of such complexes are not necessary for reaction to occur.

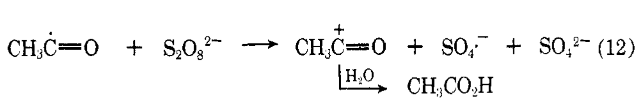
(11) J. O. Edwards, A. R. Gallapo, and E. McIsaac, *J. Amer. Chem. Soc.*, **88**, 3893 (1966).



$$(CH_3)_2C{=}O + H^+ + Ag^+ + CH_3\dot{C}{=}O \qquad (10)$$



$$O{=}C{=}O + H^+ + Ag^+ + CH_3\dot{C}{=}O \qquad (11)$$



$$CH_3\dot{C}{=}O + S_2O_8^{2-} \longrightarrow CH_3\overset{+}{C}{=}O + SO_4^{\cdot -} + SO_4^{2-} \qquad (12)$$
$$\xrightarrow{H_2O} CH_3CO_2H$$

the kinetic data for the reaction given in Tables I, II, and III and the effects of allyl acetate in retarding the reaction rates.

Cleavage of the substrates by Ag^{III} in path I is possibly significant only at the higher $[Ag^I]$ and substrate concentrations. Under these conditions, particularly in the case pinacol and the hydroxy ketone **2**, the reaction follows a rate law that is independent of the substrate concentration but is first order in $[Ag^I]$ and some higher kinetic order in $[S_2O_8^{2-}]$. This rate law is consistent with the sequence of reactions 13–15 in which formation of Ag^{III} (reaction 14) is the rate-determining step. The derived rate law for reaction 14 is given by eq 16 which indicates that the reaction is first order in $[Ag^I]$ and a kinetic order for $[S_2O_8^{2-}]$ that depends both on the extent of complexing of Ag^I with $S_2O_8^{2-}$ and the formation constant (k_{13}/k_{-13}) of the complex. If the complexing constant is low ($k_{-13} > k_{13}$), as might be expected for Ag^+ with oxygen functions, the contribution of k_{-13} to the rate of formation of Ag^{III}, and consequently the rate of cleavage by path I, may be significant and complexing of $S_2O_8^{2-}$ with Ag^I is consequently more extensive at higher $[S_2O_8^{2-}]$ and therefore the kinetic order of $S_2O_8^{2-}$ is greater at the higher concentrations of $S_2O_8^{2-}$.

$$\text{(fast) } Ag^I + xS_2O_8^{2-} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} Ag^I(S_2O_8^{2-})_x \qquad (13)$$

$$\text{(slow) } Ag^I(S_2O_8^{2-})_x + S_2O_8^{2-} \xrightarrow{k_{14}} Ag^{III} + 2SO_4^{2-} + xS_2O_8^{2-} \qquad (14)$$

$$\text{(fast) } Ag^{III} + \text{substrate} \longrightarrow Ag^{III}\text{ (substrate)} \xrightarrow{k_{15}} Ag^I + \text{products} \qquad (15)$$

$$\text{rate} = \frac{d[Ag^{III}]}{dt} = \frac{k_{13}k_{14}[Ag^I][S_2O_8^{2-}]^{x+1}}{k_{14}[S_2O_8^{2-}] + k_{-13}} \qquad (16)$$

The free-radical chain sequence for oxidative cleavage by path II is summarized in eq 17–19. This chain sequence is initiated by reaction of Ag^{III} produced in reaction 14 with Ag^I producing two Ag^{II} which start two chain sequences. Since reaction of Ag^I must compete with the substrate for Ag^{III} (reaction 15), initiation of the chain sequence by eq 20 should be favored by lower substrate concentrations. The inverse relationship of substrate concentration and the oxidative–cleavage rates suggests that reaction by the free-radical chain reaction in path II is faster than cleavage by path I. This effect is most pronounced in the reactions of pyruvic acid and is probably indicative of a faster rate of reaction of Ag^{III} with this substrate than with either pinacol or the hydroxy ketone **2**. At low $[Ag^I]$, however, the inverse rate relationship is observable with both **1** and **2** because the balance between formation of Ag^{II} by reaction 20 and interaction of the substrate with Ag^{III} is more sensitive.

$$Ag^{II} + \text{substrate} \xrightarrow{k_{17}} Ag^I + \text{product} + \text{radical} \qquad (17)$$

$$\text{radical} + S_2O_8^{2-} \xrightarrow{k_{18}} \text{product} + SO_4^{2-} + SO_4\cdot^- \qquad (18)$$

$$SO_4\cdot^- + Ag^I \xrightarrow{k_{19}} Ag^{II} + SO_4^{2-} \qquad (19)$$

$$Ag^{III} + Ag^I \longrightarrow 2Ag^{II} \qquad (20)$$

Addition of allyl acetate to the reaction mixture indicates that the chain sequence in path II is operative to a significant extent in the pinacol and hydroxy ketone reactions (Table IV). The smaller effect of allyl acetate on the rate of cleavage of pyruvic acid is consistent with the suggestion made previously that path I may be operative to a greater extent than the free-radical path II for pyruvic acid because of its rapid reaction with Ag^{III}. It is interesting to note that the reaction rates of the inhibited reactions are essentially the same, an observation that supports the suggestion that the substrate is not involved in the rate-determining processes of path I.

Table IV

Effects of Allyl Acetate on Oxidative–Cleavage Rates[a]

Substrate (M)	$[S_2O_8^{2-}]$ × 10^2	$[Ag^I]$ × 10^3	[Allyl acetate]	Rate[b]
Pinacol (0.075)	1	2.56	0	2.77
Pinacol (0.075)	1	2.56	2.5×10^{-2}	0.24
Pinacol (0.075)	1	2.56	1×10^{-1}	0.12
2-Methyl-2-hydroxy-3-butanone (0.075)	1	2.56	0	0.54
2-Methyl-2-hydroxy-3-butanone (0.075)	1	2.56	2.5×10^{-2}	0.13
2-Methyl-2-hydroxy-3-butanone (0.075)	1	2.56	1×10^{-1}	0.08
Pyruvic acid (0.075)	1	2.56	0	0.20
Pyruvic acid (0.075)	1	2.56	2.5×10^{-2}	0.12
Pyruvic acid (0.075)	1	2.56	1×10^{-1}	0.09

[a] All rates estimated from first 10% reaction of $S_2O_8^{2-}$ and are expressed in mol $l.^{-1}$ min^{-1} × 10^4. [b] Solutions buffered at pH 1.4 by 0.25 M Na_2SO_4 and 0.25 M $NaHSO_4$.

The rate laws for oxidative cleavage by path II depend on the chain sequence 17–19, the initiation process 20, and the mode of termination of the chain reaction that may be operative. The termination reactions are bimolecular interactions of chain carrying free radicals and the particular chain-carrying radicals involved in termination depend to a significant extent on the relative steady-state concentrations of these species. These concentrations are dictated both by the reaction rate constants of the chain propagating reactions and the relative concentrations of the reactants that participate in the chain sequence.[12]

It is apparent from the data in Table IV that an appreciable amount of the oxidative cleavage of pinacol and the hydroxy ketone 2 is likely occurring by path II in the reactant concentration range (high substrate and Ag^I concentration) where path I might be expected to occur. The observed oxidative cleavage rate law in this concentration range for pinacol and 2 is not only consistent for path I as indicated previously but would also be the rate law for path II under certain conditions. These conditions are met if the chain sequence is terminated by the interaction of a substrate derived radical with a sulfate ion radical. The derived rate law for

$$\text{radical} + SO_4\cdot^- \xrightarrow{k_{21}} \text{product} + SO_4^{2-} \tag{21}$$

path II if reaction 21 is the termination reaction is given by

$$\text{rate} = \left(\frac{R_i}{k_{21}}\, k_{18}k_{19}[Ag^I][S_2O_8^{2-}]\right)^{1/2} \tag{22}$$

R_i is the rate of initiation of the chain sequence. The rate of formation of Ag^{II} by reaction 20 is actually the rate of formation of Ag^{III} in reaction 14 and is given by rate eq 16. Substitution of 16 in 22 gives 23, a rate equation for path II which shows the oxidative cleavage rate is first order in $[Ag^I]$, zero order in the substrate, and some higher orders in $S_2O_8^{2-}$.

$$\text{rate} = \left(\frac{k_{13}k_{14}k_{18}k_{19}}{k_{21}(k_{14}[S_2O_8^{2-}] + k_{-13})}\right)[Ag^I][S_2O_8^{2-}]^{(x+2)^{1/2}} \tag{23}$$

Decreasing the concentration of the substrate has two effects on the course of the oxidative cleavage reaction. As pointed out earlier, partitioning of the available Ag^{III} favors reaction with Ag^I thereby increasing the amount of reaction occurring by path II relative to path I. Further, the termination of the free-radical chain sequence may take a different course at low substrate concentrations since the steady-state concentration of Ag^{II} would necessarily be greater than that encountered in higher substrate concentrations. This being the case, the sequence would be terminated by reaction 24 and the derived steady-state rate law

$$Ag^{II} + \text{radical} \xrightarrow{k_{24}} Ag^I + \text{product} \tag{24}$$

for the reaction under such conditions is eq 25. The

$$\text{rate} = \left(\frac{k_{13}k_{14}k_{17}k_{18}[Ag^I][\text{substrate}][S_2O_8^{2-}]^{(x+2)}}{k_{24}(k_{14}[S_2O_8^{-2}] + k_{-13})}\right)^{1/2} \tag{25}$$

derived rate law indicates the reaction rate is half order in both the substrate and Ag^I and is consistent with the observed rate law at low substrate concentrations.

At low $[Ag^I]$, the steady-state concentration of $SO_4\cdot^-$ is relatively greater than at higher concentrations of Ag^I. Termination of the chain sequence by reaction 26[13]

$$2SO_4\cdot^- \longrightarrow \text{termination product} \tag{26}$$

is therefore more probable at low $[Ag^I]$. The derived steady-state rate law for path II when the chain sequence 17–19 is terminated by 26 is given in 27. The

$$\text{rate} = \left(\frac{k_{13}k_{14}[Ag^I][S_2O_8^{2-}]^{(x+1)}}{2k_{26}(k_{14}[S_2O_8^{2-}] + k_{-13})}\right) k_{19}[Ag^I] \tag{27}$$

higher kinetic order of Ag^I observed at low $[Ag^I]$ is consistent with termination reaction 26 occurring at low $[Ag^I]$.

Termination of the chain sequence in a bimolecular interaction of two substrate derived radicals becomes significant if the steady-state concentration of these radicals is appreciably increased. Consequently, at low $[S_2O_8^{2-}]$, reaction 28 would be the expected path

$$2\ \text{radicals} \xrightarrow{k_{25}} \text{termination product} \tag{28}$$

for termination of the chain sequence. The derived steady-state rate law for path II when termination does occur only by 28 is given in 29. This rate law

$$\text{rate} = \left(\frac{k_{13}k_{14}[Ag^I][S_2O_8^{2-}]^{(x+1)}}{2k_{28}(k_{14}[S_2O_8^{2-}] + k_{-13})}\right)^{1/2} k_{18}[S_2O_8^{2-}] \tag{29}$$

predicts, as is observed at low $[S_2O_8^{2-}]$, that the reaction rate would be zero order in the substrate, half order in $[Ag^I]$, some some higher kinetic order in $S_2O_8^{2-}$.

It is of some significance that the observed rate laws for the oxidative cleavage reactions approach those predicted on the basis of the expected termination process when the concentration of a single reagent is appreciably decreased. At intermediate concentrations of the reagents, more than one termination reaction may be operative.

Experimental Section

Materials.—Pinacol was prepared by the procedure described by Vogel.[14] 2-Hydroxy-2-methyl-3-butanone and pyruvic acid were obtained from Aldrich and redistilled before using. Potassium peroxydisulfate (Fisher Certified Reagent) silver nitrate (Merck), sodium sulfate (Mallinkrodt Analytical Reagent), and sodium bisulfate (Baker and Adamson Reagent) were used without further purification. Allyl acetate (bp 100–102°, $n^{26}D$ 1.4011) was prepared by a Fisher ester synthesis from allyl alcohol and acetic acid.

Kinetic Measurements.—The reactions were performed in distilled water buffered to a pH of 1.4 by 0.25 *M* sodium sulfate and 0.25 *M* sodium bisulfate. The organic substrate and potassium peroxydisulfate were dissolved in the buffered solution and placed in a painted three-neck 500-ml flask. The flask was placed in a water bath maintained at 30 ± 0.1° and nitrogen was bubbled through the solution for 1 hr to remove any dissolved oxygen. An appropriate amount of 0.4 *M* silver nitrate was added and immediate reaction ensued. Aliquotes of the reaction mixture were removed at appropriate time intervals and the unreacted peroxydisulfate determined by the iodometric method described by Bartlett and Cotman.[15]

Product Distribution in Oxidative Cleavage Reactions.—A mixture consisting of 2-hydroxy-2-methyl-3-butanone (3.83 g, 0.0375 mol), potassium persulfate (6.76 g, 0.025 mol), and silver nitrate (0.106 g, 0.000625 mol) in 250 ml of water was allowed to react under a nitrogen atmosphere for 2 days. Gas chromatographic analysis of the reaction mixture on a 6 ft by $^1/_8$ in. column packed with Poropak Q (80–100 mesh) indicated the presence of 0.021 mol of acetone, 0.024 mol of acetic acid, and 0.015 mol of the unreacted hydroxy ketone. Extraction of the reaction mixture with ether afforded samples of acetic acid [mp

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[12] For discussion see E. S. Huyser, "Free-Radical Chain Reactions," Wiley, New York, N. Y., 1970, Chapter 4.

[13] The nature of the product(s) in reaction 26 can only be speculated about but may be the result of interactions of $SO_4\cdot^-$ with H_2O producing hydroxy radicals which couple yielding H_2O_2. Provided the radical products of the $SO_4\cdot^-$ interactions, other than the chain propagating reaction 19, do not become involved in the chain reaction, the kinetic consequence is a bimolecular reaction of $SO_4\cdot^-$ radicals.

[14] A. J. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, London, 1956, p 349.

[15] P. D. Bartlett and J. D. Cotman, *J. Amer. Chem. Soc.*, **71**, 1419 (1949).

(*p*-bromophenacyl ester) 82° (lit.[16a] 85°)] and acetone [mp (2,4-dinitrophenylhydrazone) 124–125° (lit.[16b] 126°)].

In a reaction of 3.3 g (0.028 mol) of pinacol with 4.87 g (0.018 mol) of potassium peroxydisulfate and 0.042 g (0.00025 mol) of silver nitrate, 2.18 g (0.018 mol) of pinacol was recovered unreacted and 1.05 g (0.018 mol, 90% of theory) of acetone was formed as determined by gas chromatographic analysis of the reaction mixture.

Reaction of 0.88 g (0.010 mol) of pyruvic acid with 4.32 g (0.016 mol) of potassium peroxydisulfate and 0.042 g (0.00025 mol) of silver nitrate yielded 0.59 g (0.0098 mol, 98% of theory) of acetic acid as determined by gas chromatographic analysis of the reaction mixture. Carbon dioxide was evolved during the course of this reaction but not measured quantitatively.

Registry No.—**1**, 76-09-5; **2**, 115-22-0; **3**, 127-17-3; peroxydisulfate ion, 15092-81-6; allyl acetate, 594-87-7; Ag$^{(I)}$, 14701-21-4.

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[16] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1956: (a) p 311; (b) p 362.

The Reductive Dimerization of Schiff Bases by Alkali Metals. Isomerization of the Dimeric Dianions

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The alkali metal induced reductive dimerization of substituted *N*-benzalanilines (ArCH=NPh) in ether solvents is examined. Particular attention is directed toward the isomerization of the diastereomeric mixture of dimeric dianions which are the primary products of the reaction. By means of cross-product experiments, it is shown that the isomerization results from an equilibrium between the dimeric dianions and the monomeric radical anion of the original *N*-benzalaniline. The observed effects of solvent and substituent groups correlate well with this conclusion.

The synthetic value of the reductive dimerization of carbonyl compounds or their derivatives is reflected in the variety of reagents which have been developed to effect this reaction.[1-10] A characteristic feature of the reaction is the formation of diastereomeric mixtures and this feature has stimulated efforts to elucidate the factors controlling the diastereomeric ratio.[11] Among the many examples of reductive dimerization, the reaction of *N*-benzalaniline with alkali or alkaline earth metals in anhydrous solvents has the intriguing feature that essentially only one diastereomer is formed, *dl*-*N*,*N'*,1,2-tetraphenylethylenediamine, under selected reaction conditions.[12,13] As has been shown,[12] the preponderance of the *dl* isomer arises from an isomerization of the diastereomeric dimeric dianions initially formed in the reductive dimerization, an isomerization which predominates in the *dl* dianion.

It was the intention of the present investigation to distinguish between the two mechanisms previously suggested[12] for the isomerization (see Scheme I). The first mechanism (path a, dissociative mechanism) depends on an equilibrium between the radical anion **2** and the dimeric dianions **3** to allow the kinetic product to isomerize to the thermodynamic one. The second mechanism (path b, carbanionic mechanism) relies on the abstraction of a benzylic proton by the basic amine anion **3**, forming a carbanion **4** which can then epimerize.

Should a mixture of two *structurally* different dimeric dianions **3** be present in solution, then the anionic mechanism would predict that the equilibrium mixture should consist essentially of the two *dl*-dimeric dianions. On the other hand, the dissociative mechanism would predict the formation of these and a cross dimer formed by the coupling of the two different radical anions present.

Such an experiment required two different diamines **5** whose anions were known to isomerize during formation and whose nmr spectra were sufficiently different that the reaction mixture could be analyzed. To optimize the formation of cross products, the *meso* isomer was preferred. In addition, a process was needed to convert the diamine to its corresponding dianion in order to induce isomerization.

With this purpose in mind, a number of substituted benzalanilines **1** were subjected to reductive dimerization with sodium in tetrahydrofuran (THF) or diethyl ether (DEE). The data pertaining to isomerization is summarized in Table I. Authentic samples of the dimeric diamines were isolated either from these reaction mixtures or from similar mixtures generated with aluminum amalgam. Table II summarizes the physical properties of the diamines and Table III the product composition from the aluminum amalgam reductions which, unlike the alkali metal reductions, contain large amounts of monomeric reduction products.

The stereochemistry of the dimeric diamines **5** is assigned on the assumption that the resonances of the benzylic protons in the *meso* isomer appear downfield from those of the *dl* isomer.[14,15] Such an assumption

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[1] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 50–77.

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