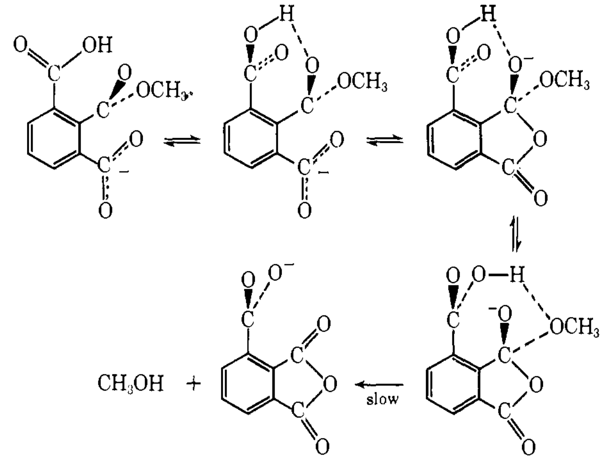
rapid do not explain the greater reactivity of un-ionized 2-methyl ester relative to the ionized ester. To postulate the inability of carboxylate anion to attack the ester is inconsistent with the observation of efficient nucleophilic carboxylate anion catalysis of phenyl hydrogen phthalate.[4] Therefore, the absence of a proton hinders the loss of methanol, and a mechanism for the monoanion reaction must involve the protonation of the departing methoxyl function by a carboxyl group or incipient hydronium ion rather than by water as must occur in the dianion reaction. Proton donation is the critical factor for determining the partitioning of the cyclic intermediate since ring opening does not require protonation but methanol elimination does require it.

A mechanism of rapid, reversible carboxylate anion cyclization and slow loss of methanol, therefore, explains the relative rates of monoanion and dianion. The pH maximum can be explained by bifunctional catalysis of the following types. One possibility, shown in Scheme III, involves attack by the carboxylate anion on the hydrogen-bonded ester function, a proton shift, and rate-limiting loss of methanol assisted by the acid group. A proton shift is unnecessary if the carboxyl group can rotate, but bonding of the carboxyl group to the methoxyl oxygen atom in the transition state is necessary. This mechanism is an example of bifunctional catalysis of tetrahedral intermediate formation and monofunctional catalysis of its breakdown.

Scheme III



Another mechanism that is less important perhaps is one of unassisted cyclization by the carboxylate anion followed by catalysis of the breakdown of the intermediate by the acid group. It differs from the previous mechanism in that cyclization occurs while the carboxyl group is hydrogen bonded to the methoxyl group or is free. This represents a type of bifunctional catalysis where each of two steps is catalyzed by single but different groups.

Alternatively, there may be concerted nucleophilic carboxylate anion cyclization and protonation of the ester carbonyl oxygen by the acid group, then breakdown of the intermediate by water in the manner shown in Scheme II. Only bifunctional catalysis of the first step occurs in this mechanism.

In conclusion, similar mechanisms were believed to be operating in all pH regions except high pH where the very reactive hydroxide ion is able to overcome the energy barrier to external attack. A mechanism of nucleophilic participation by the carboxyl group in the protonated ester and neutral ester reactions and by the carboxylate anion in the monoanion and dianion reactions is proposed. Bifunctional catalysis is not much more effective than the monofunctional catalysis by the carboxyl group observed for the neutral ester but is very effective compared to the monofunctional catalysis by the carboxylate anion observed for the dianion. This is explained by rate-limiting loss of methanol in the second step of the reaction and the necessity for protonation of the leaving group. Bifunctional catalysis is likely to be extremely effective in the hydrolysis of aryl esters or amides where the first step of the reaction is rate limiting.

The Silver Ion Assisted Solvolysis of α-Bromoisobutyrophenone[1]

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Abstract: The silver ion assisted solvolysis of α-bromoisobutyrophenone is kinetically complex. The rate equation which best fits all the data contains three terms, one first order in halide and silver ion, one first order in halide, silver ion, and hydrogen ion, and one first order in halide and second order in silver ion. Extensive amounts of rearranged products (dimethylphenylacetic acid and the ethyl ester) are observed. The kinetic and product distribution data are interpreted in terms of a mechanism involving an acid-catalyzed addition of solvent to the carbonyl group of α-bromoisobutyrophenone prior to the silver ion assisted solvolysis step.

Previous studies in our and other laboratories have been devoted to the study of the role of neighboring ketone functional groups in the solvolysis of halides and tosylates. Three different modes of neighboring group participation have been delineated. In a study of the silver ion assisted solvolysis of alkyl and aryl ω-chloro-

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(1) Submitted to the University of Notre Dame by J. P. S. in partial fulfillment of the requirements for the Ph.D. degree, 1969.

(2) (a) Alfred P. Sloan Research Fellow, 1967–1969; (b) National Aeronautics and Space Administration Trainee, 1966–1969.

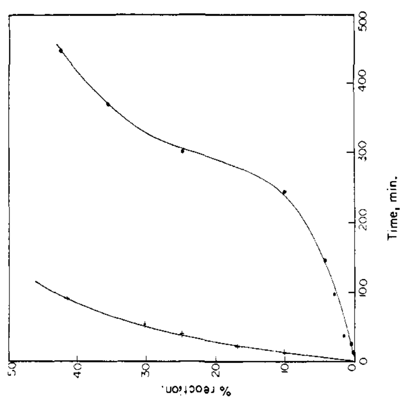
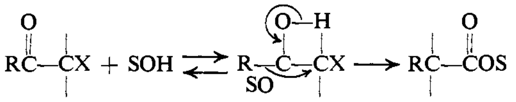


Figure 1. Solvolytic reactivity of *p*-methoxy-α-bromoisobutyrophenone in the presence of silver perchlorate ($\cdot$, [RBr] = 0.117 *M*, [Ag$^+$] = 0.072 *M*, [HClO$_4$] = 0.0 *M*) and silver perchlorate and perchloric acid (+, [RBr] = 0.0147 *M*, [Ag$^+$] = 0.0302 *M*, [HClO$_4$] = 0.40 *M*).

alkyl ketones it has been proposed that the carbonyl group participates by interaction of the electrons in the highly p-hybridized orbital on the carbonyl oxygen.[3,4] Gassman and Marshall[6] and Marshall and Brooks[7] have demonstrated that the carbonyl group may participate *via* its enol form, particularly when the substrate molecule does not allow for direct interaction by the carbonyl group.

The third mode of reactivity of ketohalides and tosylates, which are not capable of direct interaction either by the nonbonded electrons on oxygen or *via* enol formation, involves the addition of solvent to the carbonyl group followed by silver ion assisted solvolysis with rearrangement as first suggested by Cope and Synerholm.[8] Other investigators have also proposed this type


(A)

of mechanism in the solvolytic reactions of substituted ketones.[9–11]

Detailed mechanistic studies have been carried out on reactions involving carbonyl oxygen participation[3] and enol participation;[6] however, the solvent addition mechanism has not received careful attention. Studies in our laboratories on the solvolysis of substituted phenacyl halides suggested that these systems react by a direct SN2 displacement of halide by solvent.[12] No evidence was obtained indicating carbonyl oxygen participation or prior addition of solvent to the carbonyl group.[12] We have now completed a study of the silver ion assisted solvolysis of α-bromoisobutyrophenone, a system in which direct nucleophilic attack by solvent should be disfavored, and find that in contrast to the other systems previously studied the solvolysis of α-bromoisobutyrophenone is much more complex.

Results

Kinetic Analysis. Initial kinetic runs of the solvolysis of α-bromoisobutyrophenone, and the *p*-methyl and *p*-methoxy derivatives, in 75% aqueous ethanol displayed autocatalytic properties. This is illustrated rather dramatically in the case of *p*-methoxy-α-bromoisobutyrophenone in Figure 1. The autocatalysis observed in these reactions is due to the hydrogen ion which is generated as a product (see Figure 1) and is not due to the silver bromide precipitate which is formed in the reaction.[13]

A solution of *p*-methoxy-α-bromoisobutyrophenone and silver perchlorate in aqueous ethanol produces very little silver bromide over the course of 1 hr; however, the addition of a few drops of perchloric acid leads to a rapid formation of silver bromide. Subsequent kinetic runs demonstrated that the rate of the silver ion assisted solvolysis of the α-bromoisobutyrophenones was dependent on both the silver and hydrogen ion concentrations. It was also shown that α-bromoisobutyrophenone does not undergo solvolysis in the absence of silver ion (<2% in 13 days at 25° in the presence of added perchloric acid).

The dependence of the rate of solvolysis of α-bromoisobutyrophenone on the silver and hydrogen ion concentrations is in distinct contrast to the kinetic behavior of the alkyl and aryl ω-chloroalkyl ketones and the phenacyl halides which were cleanly first order in silver ion and showed no hydrogen ion catalysis.[3,12] In view of the preliminary findings, the kinetics of the solvolysis of α-bromoisobutyrophenone were determined at a constant ionic strength of 1.1 in the presence of perchloric acid (0.1–1.0 *M*) and silver perchlorate (0.01–0.091 *M*) with sufficient added lithium perchlorate to attain the desired ionic strength. The kinetic runs were followed to 50–60% completion.

The rate expression giving the most satisfactory fit of the experimental data is given in eq 1. Other rate ex-

$$\text{rate} = k_{\text{II}}[\text{Ag}^+][\text{RBr}] + k_{\text{H}}[\text{Ag}^+][\text{RBr}][\text{H}^+] + k_{\text{Ag}}[\text{Ag}^+]^2[\text{RBr}] \quad (1)$$

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(3) D. J. Pasto and M. P. Serve, *J. Amer. Chem. Soc.*, **87**, 1515 (1965).

(4) An alternative mechanistic explanation has been proposed which involves attack of solvent on the carbonyl group synchronously with, or before, participation in the ionization process.[5] We do not believe that this explanation is consistent with the experimental facts. The ρ value for the solvolysis of substituted aryl ω-chlorocaprophenone of -0.88 is not consistent with an overall mechanism involving addition of solvent to the carbonyl group. ρ values for additions to carbonyl groups are substantially positive, +1.81 for the addition of semicarbazide to benzaldehydes (B. M. Anderson and W. P. Jencks, *ibid.*, **82**, 1773 (1960)) and +1.49 for cyanohydrin formation (H. H. Jaffé, *Chem. Rev.*, **53**, 200 (1953)), thus requiring ρ for the participation–ionization step to be > -2. Such a highly negative ρ value for this step is not reasonable. Furthermore, addition of solvent to a carbonyl group is expected to be acid catalyzed (as shown by the results in this paper), and starting from zero hydrogen ion concentration would give rise to autocatalytic kinetics. Such was not the case.

(5) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms—1965," Interscience, New York, N. Y., 1966, p 55.

(6) P. G. Gassman and J. L. Marshall, *J. Amer. Chem. Soc.*, **88**, 2599 (1966).

(7) J. A. Marshall and J. P. Brooks, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, ORGN 6.

(8) A. C. Cope and M. E. Synerholn, *J. Amer. Chem. Soc.*, 72, 5228 (1950).

(9) A. C. Cope and E. S. Graham, *ibid.*, 73, 4702 (1951).

(10) C. L. Stevens and E. Farkas, *ibid.*, 74, 5352 (1952).

(11) P. G. Gassman and J. M. Hornback, *ibid.*, 91, 5817 (1969).

(12) D. J. Pasto, K. Garves, and M. P. Serve, *J. Org. Chem.*, **32**, 774 (1967); D. J. Pasto and K. Garves, *ibid.*, **32**, 778 (1967).

(13) E. D. Hughes, C. K. Ingold, and S. Masterson (*J. Chem. Soc.*, 1237 (1937)) have reported that the solvolysis of 2-*n*-octyl bromide in aqueous ethanol in the presence of silver oxide is autocatalytic with respect to the silver bromide formed in the reaction. These authors also reported that the solvolysis of 2-*n*-octyl bromide in moderately concentrated solutions of silver acetate and nitrate occurred more rapidly in the presence of freshly precipitated silver bromide. However, the use of silver perchlorate as the source of the silver ion leads to kinetically simple and clean reactions in which no autocatalytic affect by the silver halide precipitate is detected.[3,12,14]

(14) M. F. Hawthorne and R. D. Stram, *J. Amer. Chem. Soc.*, **79**, 2515 (1957).

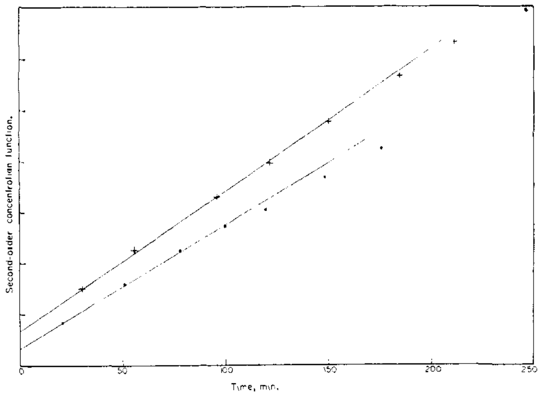

Figure 2. Second-order plots for the silver ion assisted solvolysis of α-bromoisobutyrophenone: +, run 7 of Table I; ·, run 3 of Table I.

pressions were also evaluated, in particular eq 2, in

$$\text{rate} = k[\text{Ag}^+][\text{RBr}][\text{H}^+] + k[\text{Ag}]^n[\text{RBr}] \quad (2)$$

which various values for n were evaluated. In all cases eq 1 gave the best fit of the experimental data.

The values for the composite constants k_{II}, k_{H}, and k_{Ag} were calculated in the following way. It was assumed that the solvolysis reaction was second order and could be described by eq 3. Second-order kinetic

$$\text{rate} = k_{\text{app}}[\text{RBr}][\text{Ag}^+] \quad (3)$$

plots of the data showed slight curvature (see Figure 2) but, as will be shown later, the processes first order in silver ion and bromide (overall second order) constitute 57–83% of the total reaction, except for run 11, and the second-order kinetic plots would be expected to be reasonably linear. The rate constants k_{app} were taken from the initial slope of the second-order plots as indicated in Figure 2. The values derived for k_{app} under the various experimental conditions are given in Table I.

Table I. Apparent Second-Order Rate Constants for the Silver Ion Assisted Solvolysis of α-Bromoisobutyrophenone

Run	$[\text{Ag}^+]_\text{I}$	$[\text{RBr}]_\text{I}$	$[\text{H}^+]_\text{I}$	k_{app}, l. mol^{-1} min^{-1}
1	0.0141	0.0317	0.10	0.093 ± 0.004[a]
2	0.0294	0.0134	0.20	0.128 ± 0.004
3	0.0166	0.0314	0.30	0.108 ± 0.003
4	0.0294	0.0135	0.40	0.134 ± 0.002
5	0.0180	0.0321	0.55	0.125 ± 0.003
6	0.0324	0.0140	0.70	0.152 ± 0.004
7	0.0169	0.0290	0.85	0.134 ± 0.003
8	0.0306	0.0136	1.00	0.175 ± 0.013
9	0.0100	0.0300	0.50	0.106 ± 0.007
10	0.0300	0.0300	0.50	0.131 ± 0.005
11	0.0911	0.0300	0.50	0.282 ± 0.006
12	0.0136	0.0309	0.00	0.033 ± 0.001

[a] Root mean square deviation of the experimental points from the best straight line through the points.

As the values of k_{app} were calculated for an assumed second-order kinetic equation, k_{app} may be represented as the sum of the terms in eq 4. Equation 5, obtained by rearrangement of eq 4, may be used to estimate

$$k_{\text{app}} = k_{\text{II}} + k_{\text{H}}[\text{H}^+] + k_{\text{Ag}}[\text{Ag}^+] \quad (4)$$

$$k_{\text{II}} + k_{\text{H}}[\text{H}^+]_\text{I} = k_{\text{app}} - k_{\text{Ag}}[\text{Ag}^+]_\text{I} \quad (5)$$

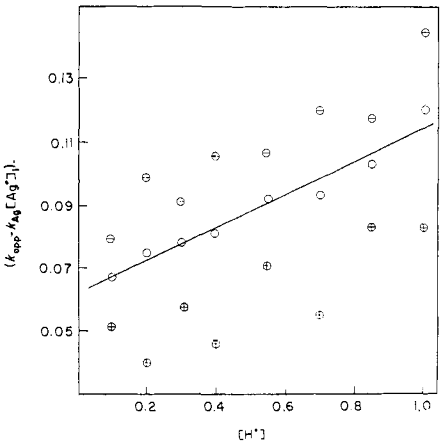

Figure 3. Plots of eq 5 with different assigned values of k_{Ag}: ⊖, $k_{\text{Ag}} = 1.00$; ○, $k_{\text{Ag}} = 1.81$; and ⊕, $k_{\text{Ag}} = 3.00$.

values for k_{II}, k_{H}, and k_{Ag} using the data in Table I for initial hydrogen and silver ion concentrations, $[\text{H}^+]_\text{I}$ and $[\text{Ag}^+]_\text{I}$. Using computer techniques, values for k_{Ag} were assigned and the values of $(k_{\text{app}} - k_{\text{Ag}}[\text{Ag}^+]_\text{I})$ were calculated and plotted *vs.* $[\text{H}^+]_\text{I}$ for runs 1–8, the optimum value for the k_{Ag} being that for which the standard deviations of the slope and intercept of the best straight line drawn through the series of points reaches a minimum. Figure 3 shows the plots obtained for values of k_{Ag} of 1.00, 1.81, and 3.00 l.^{2} mol^{-2} min^{-1}. The slope of the best straight line, with $k_{\text{Ag}} = 1.81$ l.^{2} mol^{-2} min^{-1}, is k_{H} (0.062 l. mol^{-1} min^{-1}) and the intercept is k_{II} (0.052 l. mol^{-1} min^{-1}).

The data for runs 9–11 were also used to determine the value of k_{Ag}. In these runs the initial concentrations of bromide and hydrogen ion were the same (at a constant ionic strength of 1.1), allowing us to rewrite eq 4 as eq 6. The plot of k_{app} *vs.* $[\text{Ag}^+]_\text{I}$ gave a straight

$$k_{\text{app}} = k_{\text{Ag}}[\text{Ag}^+]_\text{I} + (k_{\text{II}} + k_{\text{H}}(0.50)) \quad (6)$$

line, the slope of which is k_{Ag} (2.24 l.^{2} mol^{-2} min^{-1}) and the intercept $(k_{\text{II}} + k_{\text{H}}(0.50))$ with a value of 0.075. The value for $(k_{\text{II}} + k_{\text{H}}(0.50))$ calculated from k_{II} and k_{H} determined above is 0.088. The values for the constants determined in these two approaches are considered to be within experimental error considering the simplifying assumptions made. The fact that this latter treatment gives a straight-line plot indicates that the rate law dependence on $[\text{Ag}^+]$ does not change with changes in $[\text{Ag}^+]_\text{I}$.

The ability of the constants derived above to predict the overall rate constant (k_{calcd}) in each of the kinetic runs is illustrated by comparing the constants given in the last two columns of Table II. Excellent correspondence is observed except for run 11 in which the third-order term is dominant.

An attempt was made to clarify the intimate details of the acid-catalyzed portion of the reaction, *e.g.*, to distinguish between a dependence on hydrogen ion concentration *vs.* the acidity function H_0. Values of H_0 for perchloric acid in 75% aqueous ethanol and for perchloric acid in 75% aqueous ethanol at an ionic strength of 1.1 were determined using *o*-nitroaniline and *p*-nitroaniline as indicators (see Table III). A substantial salt effect is apparent,[15] and the values at ionic strength

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[15] This effect has been noted previously (see J. E. Leffler and E.

Table II. Comparison of Experimental and Calculated Rate Constants (l. mol^{-1} min^{-1})

Run	Contribution by: k_{II}	$k_H[H^+]_I$	$k_{Ag}[Ag^+]_I$	k_{calcd}	k_{app}
1	0.0619	0.0052	0.0255	0.093	0.093
2	0.0619	0.0104	0.0532	0.128	0.126
3	0.0619	0.0156	0.0300	0.108	0.108
4	0.0619	0.0208	0.0532	0.134	0.136
5	0.0619	0.0268	0.0326	0.125	0.123
6	0.0619	0.0364	0.0586	0.152	0.157
7	0.0619	0.0442	0.0306	0.134	0.137
8	0.0619	0.0520	0.0554	0.175	0.169
9	0.0619	0.0260	0.0181	0.106	0.106
10	0.0619	0.0260	0.0543	0.131	0.142
11	0.0619	0.0260	0.165	0.282	0.253

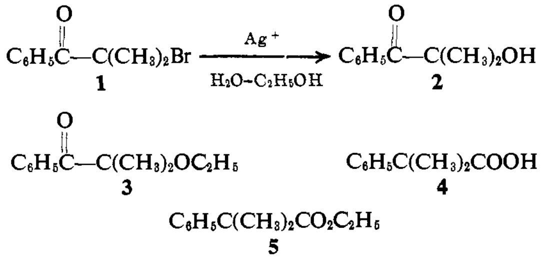
Table III. H_0 Values for Perchloric Acid in 75% Aqueous Ethanol

$LiClO_4$, mol/l.	$HClO_4$, mol/l.	H_0[a]	H_0[b]
	0.206		2.26
	0.413	1.77	1.75
	0.723	1.29	1.32
	1.03	0.97	0.98
	1.55	0.48	0.53
	2.06	0.11	0.11
	2.58	−0.39	
	3.10	−0.95	
	3.27	−1.73	
0.90	0.200		1.65
0.60	0.500		1.29
0.30	0.800		1.08

[a] Using *o*-nitroaniline as indicator. [b] Using *p*-nitroaniline as indicator.

1.1 were used for the correlation. The slope of the plot of log ($k_H[H^+]_I$) *vs.* log $[H^+]_I$ is found to be 0.94 ± 0.05, and the slope of the plot of log ($k_H[H^+]_I$) *vs.* $-H_0$ is found to be 1.09 ± 0.10. Both values are considered to be unity within experimental error and no firm conclusions can be drawn concerning the role of hydrogen ion and/or solvent in the reaction. It has been noted previously that in complex reactions the rate behavior may or may not necessarily correlate with either or both of the two functions.[16]

Product Analysis. The products formed in the silver ion assisted solvolysis of α-bromoisobutyrophenone (**1**) under conditions identical with the kinetic runs include the unrearranged alcohol **2** and ether **3** and the rearranged acid **4** and ester **5**. It was observed that **4** and **5**



$$\underset{\mathbf{1}}{C_6H_5\overset{O}{\overset{\|}{C}}\text{—}C(CH_3)_2Br} \xrightarrow[H_2O\text{-}C_2H_5OH]{Ag^+} \underset{\mathbf{2}}{C_6H_5\overset{O}{\overset{\|}{C}}\text{—}C(CH_3)_2OH}$$

$$\underset{\mathbf{3}}{C_6H_5\overset{O}{\overset{\|}{C}}\text{—}C(CH_3)_2OC_2H_5} \qquad \underset{\mathbf{4}}{C_6H_5C(CH_3)_2COOH}$$

$$\underset{\mathbf{5}}{C_6H_5C(CH_3)_2CO_2C_2H_5}$$

were interconvertible under the conditions of the reactions, but that **2** and **3** were stable under the conditions of the experiments. The sums of **2** and **3**, and of **4** and **5** were reproducible within a few per cent with total recoveries of organic material near 90% (see Table IV).

Table IV. Yield of Solvolysis Products (Per Cent)

Run	$[Ag^+]_I$	$[RBr]_I$	$[H^+]_I$	**2**	**3**	**4** + **5**	Total
1	0.027	0.0210	0.10	17.0	4.1	68.8	89.9
2	0.027	0.0208	0.10	17.5	4.5	70.0	92.0
3	0.027	0.0216	1.0	11.0	3.1	75.6	89.7
4	0.44	0.0215	0.10	18.2	6.8	66.5	91.5

The reaction conditions for determining the product distributions were chosen such that the contributions of the individual terms in eq 1, if different, would be measurable.

The calculation of the yield of products from competing processes of the same kinetic order is simple; however, such calculations for a rate equation such as eq 1 are not as simple. A computer program was written in which the total amount of product (not specified) formed from each term in eq 1 was calculated. Starting with the initial concentrations of the reactants and the best values for k_{II}, k_H, and k_{Ag}, the amount of reaction arising from each term after a small time period was calculated. New concentrations of reactants were calculated and this process was repeated out to 90% of the reaction, the amount of product arising from each term being summed. The contribution for the final 10% of the reaction was approximated by a simple distribution function based on rate constant ratios and concentrations of reactants. The normalized product yields from the three terms of eq 1 are given in Table V.

Table V. Calculated Product Yields for Each Term of Equation 1

Run	k_{II}	k_H	k_{Ag}
1, 2	63.4	5.8	30.8
3	42.9	36.6	20.5
4	7.3	0.7	92.0

Sets of simultaneous equations may now be written for the formation of **2**, **3**, and **4** + **5** for each run based on the amount of product formed from each term of eq 1. The calculated yields of each product from each process are given in Table VI. It should be noted that only phenyl-rearranged product is derived from the k_H process, whereas different quantities of unrearranged products arise from the k_{II} and k_{Ag} processes.

Table VI. Calculated Yields of **2**, **3**, and **4** + **5** from Each Term of Equation 1

Process	**2**	**3**	**4** + **5**
k_{II}	19.7	3.5	76.8
k_H	−1.3	1.1	100.2
k_{Ag}	20.0	7.8	72.2

Discussion

The kinetic results outlined in the preceding section of this article show that α-bromoisobutyrophenone does not undergo either a direct unassisted solvolysis or a direct silver ion assisted solvolysis. The autocatalysis of the solvolysis reaction, and the dramatic increase in the rate of solvolysis in the presence of perchloric acid, indicate that **1** must be undergoing an acid-catalyzed conversion to a more reactive intermediate. We be-

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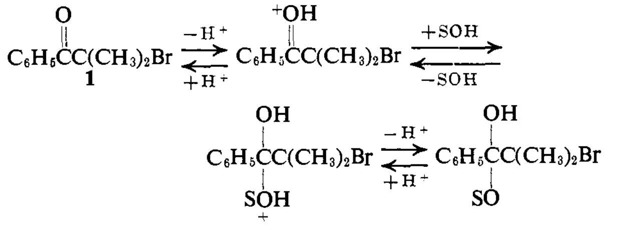
E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 276).

(16) F. A. Long and M. A. Paul, *Chem. Rev.*, 57, 935 (1957).

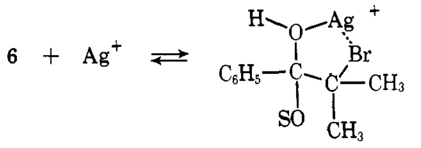
lieve that the primary role of the hydrogen ion is the catalysis of the addition of a molecule of the solvent to the carbonyl group (eq 7) to give intermediate **6** (or even possibly the diethyl ketal in subsequent steps).

The dependence of each term of the proposed kinetic equation requires that no one of the steps in eq 7 is solely rate determining. The possibility that the addition of solvent to the carbonyl is partially rate determining was explored; however, such a mechanistic scheme leads to terms in the kinetic equation with a negative silver ion order. Although assumptions must be made regarding the relative magnitudes of the various rate and equilibrium constants in such a scheme, it appears unlikely that the addition of solvent to the carbonyl group is partially rate determining in view of the observation that silver ion always leads to an enhancement of the rate of the reaction and not a rate decrease as would arise from a negative-order silver ion contribution.



$$\underset{\mathbf{1}}{C_6H_5\overset{O}{\overset{\|}{C}}C(CH_3)_2Br} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} C_6H_5\overset{^+OH}{\overset{\|}{C}}C(CH_3)_2Br \underset{-SOH}{\overset{+SOH}{\rightleftarrows}} C_6H_5\overset{OH}{\overset{|}{\underset{\underset{+}{SOH}}{\underset{|}{C}}}}C(CH_3)_2Br \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} C_6H_5\overset{OH}{\overset{|}{\underset{SO}{\underset{|}{C}}}}C(CH_3)_2Br \quad (7)$$

6



(8)

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Product forming steps are as follows

k_{II} term

$$\mathbf{6} + Ag^+ \longrightarrow \mathbf{2} + \mathbf{3} + \mathbf{4} + \mathbf{5}$$

or

$$\mathbf{7} \longrightarrow \mathbf{2} + \mathbf{3} + \mathbf{4} + \mathbf{5}$$

k_{AG} term

$$\mathbf{7} + Ag^+ \longrightarrow \mathbf{2} + \mathbf{3} + \mathbf{4} + \mathbf{5}$$

k_H term

$$\mathbf{6} + Ag^+ + H^+ \longrightarrow \mathbf{4} + \mathbf{5}$$

or

$$\mathbf{7} + H^+ \longrightarrow \mathbf{4} + \mathbf{5}$$

The k_{II} term of eq 1 is consistent either with a direct silver ion assisted solvolysis of the solvent–addition product **6** (eq 9), or by reaction of **6** with silver ion to produce a complex depicted as **7** which then undergoes decomposition to products (eq 10). A distinction between these two possibilities is not possible. The reaction of intermediate **7** with a second silver ion to give products gives rise to the k_{AG} term in eq 1. The origin of the k_H kinetic term in eq 1 is not obvious. It is conceivable that a hydrogen ion may replace the second silver ion in eq 11, to give eq 12. The observed differences in product distribution from the k_{AG} and k_H terms may be due to the position of interaction of the silver ion or hydrogen ion with **7** in eq 11 and 12. Other mechanistic schemes are possible; however, with the present data the above scheme fits the data satisfactorily.

The unique aspect of the silver ion assisted solvolysis of **1** is the presence of a term in the kinetic equation second order in silver ion. To the authors' knowledge this is the first observation of a distinct kinetic term second order in silver ion in the silver ion assisted solvolysis of an organic halide. Numerous examples of reactions with higher than unity, nonintegral orders in silver ion have been observed; however, these reactions involved the use of silver salts which are highly associated as ion aggregates in solution (for example, silver acetate and nitrate).[17]

The proposal of distinct competing first and second order in silver ion terms, however, is not entirely new. Saville[18] has shown that the silver ion assisted displacement of ethylsulfide anion by fluoride in diethyl ethylphosphonothiolate, and the silver ion assisted solvolysis of unsaturated alkyl sulfides follows the rate law

$$\text{rate} = \alpha[\text{substrate}][Ag^+] + \beta[\text{substrate}][Ag^+]^2$$

The present system is unique from the others studied previously, and is somewhat similar to the systems studied by Saville. The oxygen functional groups in **6** provide a means of intramolecular stabilization for complex formation (**7**), a feature not present in the vast majority of the other organic halides previously studied. In addition, the methyl groups inhibit the direct nucleophilic displacement of the silver ion complexed bromide by solvent[12] (generally a lower energy reaction pathway) as well as sterically interfering in solvation stabilization of the transition state normally encountered in the silver ion assisted solvolysis reactions.

Experimental Section

Measurement of Kinetics. Solutions of perchloric acid in 75% by weight aqueous ethanol were prepared by the addition of calculated quantities of standardized aqueous perchloric acid and water to absolute ethanol. These solutions were standardized by titration with standard base. To these solutions were added silver perchlorate and lithium perchlorate to obtain solutions of the desired silver ion concentration and ionic strength. Weighed quantities of α-bromoisobutyrophenone were dissolved in 50.0 ml of 75% by weight aqueous ethanol. Aliquots of the acidic silver perchlorate (5.0 ml) and α-bromoisobutyrophenone (5.0 ml) solutions were added to 15-ml ampoules. The ampoules were sealed and placed in a constant-temperature bath at 25.00°. Ampoules were periodically removed and the contents removed and added to 25 ml of water. The amount of silver ion present was determined by potentiometric titration with standard potassium iodide.

Product Identification. Solutions of α-bromoisobutyrophenone, silver perchlorate, and perchloric acid in 75% by weight aqueous ethanol were prepared as described above. The reaction mixtures were allowed to stand at 25.0° for several days. The reaction mixtures were poured into water and were extracted with five 50-ml portions of ether. The combined ether extract was dried over anhydrous magnesium sulfate and the ether was removed under reduced pressure. To each product mixture was added a weighed amount of diphenyl ether and the resultant admixture was analyzed by glpc on a 20% Carbowax 20M on Chromosorb G column at 165°. Under these conditions the yields of α-hydroxyisobutyrophenone,[19] α-ethoxyisobutyrophenone, and ethyl α,α-dimethylphenylacetate were determined. The admixture was then dissolved

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[17] For example, see ref 13.

[18] B. Saville, *J. Chem. Soc.*, 4624 (1961); 4062 (1962).

[19] α-Hydroxyisobutyrophenone undergoes a reversible transformation to 3-hydroxy-3-phenyl-2-butanone under the conditions of the glpc analysis. The absence of 3-hydroxy-3-phenyl-2-butanone in the original crude reaction mixture was demonstrated by nmr analysis.

in a few milliliters of ether and a slight excess of ethereal diazoethane was added, converting the α,α-dimethylphenylacetic acid to its ethyl ester. The solvent was again removed under reduced pressure and the resultant mixture was again analyzed by glpc as above. The increase in the yield of ethyl α,α-dimethylphenylacetate represents the yield of the acid originally present in the reaction mixture.

α-Hydroxyisobutyrophenone. To 100 ml of a 1.8 *M* solution of potassium hydroxide in ethanol was added 2 g of α-bromoisobutyrophenone. The reaction mixture was stirred for 1 hr and was then added to 300 ml of water and was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave α-hydroxyisobutyrophenone as a viscous, colorless liquid with bp 63–68° (0.3 mm) (lit.[9] bp 101–106° (6 mm)). The ir and nmr spectra were consistent with the assigned structure.

α-Ethoxyisobutyrophenone. Treatment of α-bromoisobutyrophenone with sodium ethoxide in absolute ethanol did not produce α-ethoxyisobutyrophenone; it produced instead only 1-ethoxy-1,2-oxido-2-methyl-1-phenylpropene.[20]

The α-ethoxyisobutyrophenone was isolated by preparative glpc of a solvolysis reaction mixture. The nmr spectrum of **3** showed a triplet at δ 1.08 (3 H), singlet at 1.47 (6 H), quartet at 3.31 (2 H), and multiplets at 7.4 and 8.2 (5 H total).

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Halogen Abstraction Studies. II. Free-Radical Abstraction of Iodine from Aliphatic Iodides. Evidence to Support Anchimeric Assistance by Neighboring Halogen in Homolytic Reactions[1]

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Abstract: The rate of abstraction of iodine from a series of aliphatic iodides relative to the rate of abstraction of bromine from bromotrichloromethane is reported. The influence of inductive effects on the rate of abstraction from various primary iodides is illustrated by a quite good correlation of relative reactivities with Taft polar substituent constants exhibiting a ρ value of +0.184. Both β-bromine and γ-iodine substituents cause a rate enhancement for abstraction of iodine over and above that anticipated from inductive effects alone while a β-chlorine substituent exhibits rather normal behavior. These results are discussed in terms of anchimeric assistance by the former two neighboring halogens in the homolytic abstraction process. A comparison of the present iodine abstraction results with hydrogen abstraction data by the phenyl radical is also presented.

We recently reported the facile abstraction of iodine from substituted iodobenzenes by the phenyl radical and noted that this process contrasts with hydrogen abstraction reactions in that a positive ρ value is observed in a Hammett correlation.[3] This indicates that there is a substantial difference in charge distribution for the two transition states with the halogen abstraction process producing anionic character on the carbon from which the iodine is being removed (eq 1),

$$\mathrm{R{-}I} + \cdot\mathrm{Rad} \longrightarrow [\mathrm{R}^{\delta\cdot-}\text{---}\mathrm{I}\text{---}{}^{\delta\cdot+}\mathrm{Rad}]^{\ddagger} \longrightarrow \mathrm{R}\cdot + \mathrm{I{-}Rad} \qquad (1)$$

while cationic character is produced in hydrogen abstraction reactions (eq 2). Although there is a paucity

$$\mathrm{R{-}H} + \cdot\mathrm{Rad} \longrightarrow [\mathrm{R}^{\delta\cdot+}\text{---}\mathrm{H}\text{---}{}^{\delta\cdot-}\mathrm{Rad}]^{\ddagger} \longrightarrow \mathrm{R}\cdot + \mathrm{H{-}Rad} \qquad (2)$$

of information available concerning electronic effects on halogen abstraction reactions, numerous hydrogen abstraction reactions have been reported, all of which occur more readily when electron-donating substituents are located on the substrate from which the hydrogen is being removed.[3,4]

We presently wish to report a study of the abstraction of iodine from a series of aliphatic compounds which, similar to the aromatic iodides,[3] produces a positive ρ value in a Taft correlation illustrating the generality of substituent effects on halogen abstraction reactions. The divergence from the correlation by the aliphatic iodides with β-bromo and γ-iodo substituents suggests that anchimeric assistance to abstraction of iodine by these neighboring groups is indeed authentic.[5]

Results

The phenyl radicals were generated by decomposition of phenylazotriphenylmethane (PAT) at 60.0 ± 0.1° and the $k_{\mathrm{I}}/k_{\mathrm{Br}}$ results listed in Table I are presented as the relative reactivity of iodo compound per molecule of bromotrichloromethane calculated from eq 3. The

$$k_{\mathrm{I}}/k_{\mathrm{Br}} = \frac{[\mathrm{C_6H_5I}][\mathrm{CBrCl_3}]}{[\mathrm{C_6H_5Br}][\mathrm{RI}]} \qquad (3)$$

values are virtually insensitive to the PAT concentration and the ratio of substrate to bromotrichloromethane; estimated reliability is ±5%. The combined yields of iodobenzene and bromobenzene typically averaged 80–90% based on PAT. Bromotrichloromethane is used as the reference solvent in the present study rather than carbon tetrachloride as for the aromatic iodides[3] be-

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(2) National Science Foundation Undergraduate Research Participant, Summer 1969.

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