Formation and Decomposition of Positive Iodine Esters of Carboxylic Acids

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Silver propionate and iodine in the molar ratio 3:2 react quantitatively to form $(C_2H_5COO)_3I$. In saturated hydrocarbon solvent, this compound decomposes to ethyl iodide and unidentified other products with a half-life of several days in the dark at room temperature. The reaction is accelerated by light. Excess iodine causes a more rapid decomposition that is also accelerated by light and that may involve intermediate formation of C_2H_5COOI. The ethyl iodide formed in this more rapid decomposition contains iodine that has been isotopically equilibrated with the added iodine, and even a large excess of elementary iodine fails to produce ethyl iodide quantitatively from the propionyl groups of the original iodine(III) ester. Concentrations of ethyl iodide and of positive iodine undergo peculiar coupled fluctuations during the initial stages of the reaction, and ethyl iodide is consumed as well as produced during certain stages of the reaction. The system is too complex to provide information about geminate recombination during the decomposition of propionyl hypoiodite.

Some organic molecules dissociate in solution to form stable molecules and pairs of radical fragments that can either undergo geminate reaction or diffuse apart. The products of reaction under various conditions can be used to determine the probability that these fragments will become separated by diffusion.

Compounds studied in this way include the azonitriles,[1] R—N=N—R, and the aliphatic acyl peroxides,[2,3] $(RCOO)_2$. The acyl hypoiodites, RCOOI, should decompose similarly to yield alkyl iodide and carbon dioxide. If such a decomposition were carried out in a solution containing isotopically labeled elementary iodine, the alkyl iodide formed by geminate recombination of radical fragments would be unlabeled, while radicals that escaped by diffusion would form labeled alkyl iodide.

Although alkyl hypoiodites have not been isolated, they have been postulated as intermediates during the reaction of iodine with the silver salts of carboxylic acids. The literature on this reaction and the mechanistic proposals have been reviewed fairly recently.[4-6]

We report here some additional studies of the reaction that provide new information of mechanistic value even though they provide little insight on the specific problem of geminate recombination.

Results

Formation of Positive Iodine Esters.—Equimolar amounts of solid silver propionate and iodine in hexane solvent could be expected to react according to the equation

$$C_2H_5COOAg + I_2 \longrightarrow C_2H_5COOI + AgI \qquad (1)$$

However, reactants in these proportions never produced solutions containing significant amounts of species capable of oxidizing aqueous iodide. As is shown below, propionyl hypoiodite decomposes rapidly at room temperature and probably was destroyed as rapidly as it was formed.

If the molar ratio of silver propionate to iodine is increased from 1.0 to 1.5, the observations of Oldham and Ubbelohde[7] suggest the reaction

$$3C_2H_5COOAg + 2I_2 \longrightarrow (C_2H_5COO)_3I + 3AgI \qquad (2)$$

Reaction under these conditions was somewhat accelerated by light and took place quantitatively in sixty to one hundred and fifty minutes at room temperature. The stoichiometry was confirmed to within about 2% by radiochemical procedures (which showed that one quarter of the initial iodine remained in the now colorless hexane solution) and by hydrolysis of the iodine(III) tripropionate to iodate according to the equation

$$5(C_2H_5COO)_3I + 9H_2O \longrightarrow 3HIO_3 + I_2 + 15C_2H_5COOH \qquad (3)$$

The existence of the iodate was confirmed both by reducing with sulfite and titrating the resulting iodide with silver nitrate and also by reducing with iodide and titrating with thiosulfate. The iodide–thiosulfate procedure was used in the subsequent studies of the decomposition reaction.

Since each mole of iodate requires six equivalents of thiosulfate for titration, and since the iodine formed in equation 3 remains in the hexane layer, each ten oxidizing equivalents of iodine(III) initially present produce nine oxidizing equivalents (as iodate) in the aqueous layer and one oxidizing equivalent (as elementary iodine) in the hexane layer.

Decomposition of Positive Iodine Esters.—Dry hexane solutions of iodine(III) tripropionate decomposed slowly, and the reaction could be followed conveniently by measuring the oxidizing titer of

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[2] M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

[3] D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959).

[4] J. Kleinberg, *Chem. Rev.*, **40**, 381 (1947).

[5] R. G. Johnson and R. K. Ingham, *ibid.*, **56**, 219 (1956).

[6] C. V. Wilson, "Organic Reactions," Vol. IX, John Wiley and Sons, New York, 1957, p. 332.

[7] J. W. H. Oldham and A. R. Ubbelohde, *J. Chem. Soc.*, 368 (1941).

the iodate formed by treating an aliquot with water as indicated in equation 3.

The rate of decomposition in the dark was about one eighth that under normal laboratory illumination. In the illuminated solution, the iodine concentration remained very low, and the decomposition produced ethyl iodide. In the dark, the ethyl iodide concentration remained constant, and the decomposition produced iodine. Since the reaction was only followed about 30% of the way to completion, the kinetics were not established with certainty. However, the data seemed to be fitted best by the assumption of first order or less dependence on iodine(III) tripropionate. The apparent first order rate constant in the dark at 25° was 1.34×10^{-6} sec.$^{-1}$, corresponding to a half-life of about six days.

The decomposition reaction is obviously complex. Iodine atoms can accelerate at least one possible path and are consumed in the process.

Effects of Added Iodine.—If excess elementary iodine were added to a solution of iodine(III) tripropionate, the data of Oldham and Ubbelohde[7] suggest that the equilibrium

$$(C_2H_5COO)_3I + I_2 \rightleftarrows 3C_2H_5COOI \qquad (4)$$

should be established. An analogy with equation 3 predicts that propionyl hypoiodite should also disproportionate with water according to the equation

$$5C_2H_5COOI + 3H_2O \longrightarrow HIO_3 + 2I_2 + 5C_2H_5COOH \qquad (5)$$

Of the ten oxidizing equivalents of iodine(I) on the left side of equation 5, six will be present in the aqueous layer as iodate and four will be present in the hexane layer as additional iodine. Hence equation 5 predicts a ratio of 1.5 for oxidizing equivalents formed in aqueous and hexane layers compared to the ratio of 9.0 predicted by equation 3 and observed in the absence of excess iodine.

Our experiments failed to confirm equilibrium 4. When excess iodine was added to solutions of $(C_2H_5COO)_3I$, the iodine color faded and the rate of loss of oxidizing titer greatly accelerated. The reaction was fastest in solutions exposed to light, but even in the dark the half time for decomposition was reduced from a few days to a few hours. When water was added, the ratio of equivalents of aqueous oxidizing titer per equivalent of additional iodine in hexane fell from nine but usually did not go much below four. Only occasionally and with large excess of iodine did the ratio approach the 1.5 predicted by equation 5.

If concentrations of individual species were computed by assuming that equations 3 and 5 described the effects of water and that the only oxidizing species present were those in equilibrium 4, the calculated equilibrium constant decreased as a run progressed. This behavior would be expected if the rate of decomposition of C_2H_5COOI were comparable to or greater than the rate of equation 4 from right to left so that the equilibrium could not be established. A question about the analytical method is raised in the Discussion, but we do not see how the data can be accommodated to the establishment of equation 4 as a true equilibrium.

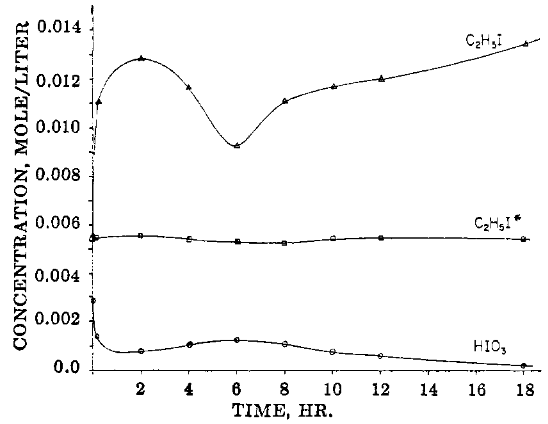

Fig. 1.—Concentrations of species following dark addition of iodine to solution of $(C_2H_5COO)_3I$.

Molar ratio of added iodine to initial $(C_2H_5COO)_3I$, 4.80:1 Concentration of HIO_3 = moles of this substance extracted with water per liter of hexane solution so treated

The situation is even more complex than is suggested by the above discussion. Figure 1 illustrates the subsequent behavior when unlabeled iodine solution was added in the dark to a solution of iodine(III) tripropionate that had been prepared with labeled I^{131}. Concentrations indicated at zero time are the ones that would have been observed if the dilution had been made with the same volume of hexane instead of with the iodine solution. If all of the positive iodine were initially in the +3 state, the molar ratio of added iodine to initial $(C_2H_5COO)_3I$ was 4.80 to 1.

As Fig. 1 shows, immediately after the iodine was added, the titer of water extractable HIO_3 fell rapidly, and the concentration of ethyl iodide rose from 0.00561 *M* to 0.0111 *M*. This concentration is more than the 0.01040 *M* expected if only the iodine in the initial $(C_2H_5COO)_3I$ were converted to ethyl iodide. The additional ethyl iodide was almost free of I^{131}; the iodine from which it was formed must have been isotopically equilibrated with the added iodine.

This initial reaction was followed by another that consumed ethyl iodide and increased the titer of water extractable HIO_3. When this reaction was over, the ethyl iodide concentration increased again while the oxidizing titer fell with a half life of about five hours (compared to six days in the absence of added iodine). The final concentration of ethyl iodide was only about two thirds of the theoretical maximum of 0.0200 *M* based on ethyl groups in the original propionate.

It is tempting to decide that the apparent maxima and minima in Fig. 1 are artifacts arising from analytical errors and that they only happen to coincide in time. However, the procedures were carefully verified in tests of apparent stoichiometry, and the analyses at each time in Fig. 1 added to the same total iodine content of the system with a total spread of 2.3%. Moreover, the same pattern was observed repeatedly. When the added excess iodine did not greatly exceed the iodine(III) ester, the maxima and minima were ripples that scarcely seemed real except that HIO_3 and ethyl iodide always changed concentrations in opposite directions. When the added iodine was in large excess, the fluctuations were large, as illustrated in Fig. 1. Sometimes the concentrations showed two positions of relative maximum for HIO_3 instead of the one shown here. Reproducibility of supposedly duplicate runs was far from satisfactory.

Effects of Added Ethyl Iodide.—Ethyl iodide was expected to be an unreactive product in this system. Results like those in Fig. 1 suggest that the role of ethyl iodide is far from passive. Although its concentration usually increased during a run, it was consumed during some runs in the dark at low iodine concentration. One solution of iodine (III) tripropionate to which about 0.01 *M* ethyl iodide was added decomposed in the dark several times faster than did one to which no addition had been made.

Discussion

Both the formation and decomposition reactions are photochemically accelerated. Radical processes can obviously make major contributions to these reactions, but we cannot exclude the possibility of parallel nonradical mechanisms.

During all of our initial thinking, ethyl iodide was assumed to be an inert product in this system. Observations like Fig. 1 require revision of this assumption. The reaction

$$C_2H_5\cdot + C_2H_5I \longrightarrow C_2H_6 + C_2H_4 + I\cdot \qquad (6)$$

is approximately thermoneutral and may well have a rather low activation energy. The photochemical observations demonstrate that iodine atoms can accelerate the decomposition of iodine(III) tripropionate. A possible reaction is

$$I\cdot + (C_2H_5COO)_3I \longrightarrow 2C_2H_5COOI + C_2H_5\cdot + CO_2 \qquad (7)$$

Reactions 6 and 7 provide a chain process by which the conversion of iodine(III) to iodine(I) ester can induce decomposition of ethyl iodide. Since the iodine(I) ester decomposes the more rapidly, decomposition of ethyl iodide could be accelerated during some stages of the reaction. It is even possible to imagine the reactants in equation 7 to form products that led to chain branching.

It is less easy to account for the observed increases in the apparent HIO_3 measurements. It is very hard to see how the total oxidizing power of the hexane solution could increase during any stage of the reaction. Our experiments determined water-extractable oxidizing material capable of oxidizing iodide. When the only oxidizing species in the hexane was iodine(III) tripropionate, we demonstrated that HIO_3 was the only oxidizing agent, but equation 3 shows that 10% of the potential oxidizing power was not extracted by water. If the hexane layer contains propionyl hypoiodite, 40% of its potential oxidizing power is not extracted by water.

Hence, the water-extractable oxidizing power would be increased by any process that formed iodine(III) ester at the expense of iodine(I) ester. However, it is hard to interpret the data in this way because the increases in apparent HIO_3 occur at precisely the times when the consumption of ethyl iodide is presumably associated with conversion of (III) ester to (I) ester.

An alternative possibility is that propionyl hypoiodite is water extractable as such. It would presumably oxidize iodide by the reaction

$$C_2H_5COOI + I^- \longrightarrow C_2H_5COO^- + I_2 \qquad (8)$$

and *all* of the oxidizing power of the iodine(I) ester would then become water-extractable. Although this interpretation could explain many of our observations, a few increases in water-extractable oxidizing power were too great to be explained in this way We see no alternative explanations without proposing additional intermediates such as iodine(II) esters.

These experiments were undertaken to obtain information about the dissociation

$$C_2H_5COOI \longrightarrow C_2H_5\cdot + CO_2 + I\cdot \qquad (9)$$

Previous work[1-3] suggests that a significant fraction of such dissociations should lead to geminate recombination. However, Fig. 1 shows that when a solution of isotopically labeled $(C_2H_5COO)_3I$ and ethyl iodide is treated with an excess of unlabeled elementary iodine, little additional labeled ethyl iodide is produced. This observation can be interpreted to indicate that reaction 9 is followed by very little geminate recombination. Alternative interpretations are that the destruction of labeled ethyl iodide by reaction 6 approximately balanced geminate recombination, that C_2H_5COOI exchanged rapidly with elementary iodine, or that decomposition did not occur by reaction 9 but by some other process such as

$$C_2H_5COOI^* + I\cdot \longrightarrow C_2H_5I + CO_2 + I^*\cdot \qquad (10)$$

The system is obviously too complex to permit easy kinetic measurements of the type that could eliminate some of these alternatives. We are therefore abandoning further study of these reactions. We would be happy to make our detailed data available to anybody interested in further study of these peculiar reactions.

Experimental

Materials.—Dry silver propionate was prepared from the acid by standard procedures.

Resublimed reagent grade iodine was used without further purification. Solutions could be labeled with carrier-free I^{131} obtained from the Oak Ridge National Laboratory.

The saturated hydrocarbon solvent was mostly hexane. It was prepared from Skellysolve B by treatment with fuming sulfuric acid. Tests with I^{131} indicated that different preparations contained impurities capable of reacting with no more than 6×10^{-6} mole/l. of iodine.

Procedure.—Because of the extreme sensitivity to moisture of iodine(III) tripropionate, solutions were dried over phosphorus pentoxide and all experiments were conducted in an atmosphere of dry carbon dioxide. Samples of solid silver propionate were treated with hexane solutions of iodine, and the resulting silver iodide was removed by filtration during transfer of the solution to a thermostated flask that was kept in the dark under dry carbon dioxide. Aliquots could be withdrawn at appropriate times for analysis.

Analytical Procedures.—Concentrations of I^{131} were determined with thin-walled Geiger tubes. Empirical corrections were applied because of different efficiencies for counting iodine in water and in hexane solution. Counting procedures could be used to determine number of moles of iodine in a particular phase regardless of its chemical form.

Elementary iodine in hexane was determined with a Beckman DU spectrophotometer.

Ethyl iodide was also determined spectrophotometrically. The molar extinction coefficient of 451 ± 5 at 259 mμ agreed well with the value reported by Scheibe.[8] The presence of this compound in a reacted mixture was also confirmed by forming the ethyl 3,5-dinitrobenzoate and taking a mixed melting point with the derivative prepared from commercial ethyl iodide.

As has been indicated above, positive iodine esters were determined by shaking the hexane solution with water, adding an excess of acid and iodide to the aqueous layer, and titrating with thiosulfate. In some experiments in which the hexane layer contained only iodine(III) ester, the hexane layer was also reduced with aqueous sulfite and titrated with silver nitrate. The combined argentometric and iodometric procedures demonstrated that iodate was the only iodine containing species present in the aqueous extract.

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Alkaloids of *Geissospermum vellosii*. Isolation and Structure Determinations of Vellosimine, Vellosiminol, and Geissolosimine

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By systematic fractionation of the alkaloid-rich pH 7 fraction[2] from *G. vellosii* three new alkaloids, *viz.*, vellosimine, vellosiminol, and geissolosimine, have been isolated. Vellosomine and vellosiminol are indoles, and by n.m.r. studies and comparison with known alkaloids, have been shown to have structures I and III, respectively. Geissolosimine (formerly called D_2[2]) is a dimeric alkaloid and is cleaved by acid to the indole, vellosimine, and the indoline, geissoschizoline. From this cleavage reaction, its reconstitution from vellosimine and geissoschizoline, and its n.m.r. spectrum, geissolosimine has been assigned structure VII.

A detailed procedure has been described[2] for the separation of the *Geissospermum vellosii* alkaloids into various fractions by systematic liquid-liquid extraction at a series of different pH's. From the alkaloid-rich pH 7 fraction, geissospermine was isolated, usually by crystallization, and large-scale chromatography on alumina then was applied to the residual material. In this way, a number of other alkaloids were isolated, the chief one being alkaloid D_2. By further refinement of the pH 7 fraction, we have isolated two additional crystalline alkaloids. These new alkaloids, vellosimine and vellosiminol, and geissolosimine (alkaloid D_2) are the subject of the present report.

Isolation.—The large amounts of material accumulated after removing geissospermine from the pH 7 fraction made detailed alumina chromatography quite unappealing as a fractionation procedure. Instead, a pass through a short alumina column first was applied and this clearly removed about one fourth of the material as crystalline geissoschizoline.[2] The remaining three fourths was subjected to systematic, continuous liquid-liquid extraction at pH 6, 6.6, and 10. From the pH 10 fraction, more geissoschizoline was isolated, and the pH 6.6 fraction yielded additional geissospermine. The pH 6 fraction, originally obtained by extraction with ether, now was separated into two portions by extraction with benzene at pH 4.9, fraction 1, and ether at pH 7, fraction 2.

Further purification of fraction 2 by chromatography on alumina was fruitful and resulted in the isolation of two crystalline minor alkaloids, vellosimine and vellosiminol. Geissolosimine was not isolated anew; it was the material (alkaloid D_2) obtained by the previous procedure.[2]

Structure Determinations.—Vellosimine has the molecular formula $C_{19}H_{20}N_2O$ and an ultraviolet

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[1] National Institutes of Health Predoctoral Fellow.

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