Definitely to prove the correctness of the sequence, the compound $CF_3CCl{=}CClCF_3$ was quantitatively oxidized by our previously reported procedure,[11] and two moles of $CF_3COOH$ were obtained.

All compounds were purified in the manner and to the degree shown in our preceding papers, and their physical properties were measured with the accuracy denoted in the following table; they were analyzed for chlorine content at significant stages and found correct within 0.2%.

## Summary

Hydrogen atoms in alpha position to a $CF_2$ or a $CF_3$ group are difficult to replace with chlorine. In order of difficulty, the following sequences were observed: $CH_3CF_2CF_2CH_3$ to $CH_3CF_2CF_2CCl_3$ to $CCl_3CF_2CF_2CCl_3$; $CF_3CH_2CF_2CH_3$ to $CF_3CH_2CF_2CCl_3$ to $CF_3CCl_2CF_2CCl_3$; $CF_3CH_2CF_3$, no chlorination observed. Advantage was taken of directed chlorination and of the acid character of hydrogen atoms alpha to a fluorinated group to synthesize $CF_3CCl{=}CClCF_3$ and $CF_3CCl_2CCl_2CF_3$ by a sequence of very efficient reactions. In $CHF_2CH_3$, chlorination affects the hydrogen of the $CHF_2$ group preferentially.

COLUMBUS, OHIO RECEIVED JULY 6, 1945

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[11] Henne, Alderson and Newman, THIS JOURNAL, **67**, 918 (1945).

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[COMMUNICATION NO. 1046 FROM THE KODAK RESEARCH LABORATORIES]

# Photographic Development by Ferrous Iron in Alkaline Solution

BY T. H. JAMES

In a previous paper,[1] it was shown that the rate of development of a typical photographic positive material in a very dilute ferro-oxalate solution decreases with increasing *p*H over the range 4.0 to 7.5. This decrease in rate is caused by a charge-barrier effect originating in the gelatin, and operating to oppose the approach of the negatively charged ferro-oxalate ion to the surface of the silver halide grains. In the presence of considerable amounts of neutral salt, such as potassium nitrate, the gelatin charge-barrier is largely removed, and the development rate becomes almost independent of the *p*H. The curves representing rate as a function of *p*H in the presence and absence of the added salt cross at the isoelectric point of the gelatin. From the magnitude of the salt effect and the accuracy of the development-rate determinations, it appears that the isoelectric point (in the finished film) of a gelatin sample can be determined to within 0.1 by this method, providing the isoelectric point lies below 7.5. However, a serious complication arises in the use of the ferro-oxalate developer at higher *p*H values. In the previous investigation, some data were obtained for a gelatin having an isoelectric point of about 8.0. The rate curves did cross near the isoelectric point, but the absolute values of the development rates showed a marked increase between *p*H 8 and 8.5. The present paper is concerned with the cause of this rather surprising increase in the development rate.

## Experimental

**Materials and Procedure.**—The developers were prepared from oxygen-free component solutions, and all development operations were carried out at 20° in an atmosphere of tank nitrogen which had been freed from oxygen. The apparatus and procedure were essentially those described previously.[2] The photographic material in most of the work was a normal motion-picture positive film. The silver halide was the bromide, with only a very small addition of iodide, and the gelatin (lime-process) isoelectric point was at 4.9.

## Results

The increase in rate with *p*H above 8.0 proved to be just as great with the photographic material prepared from lime-process gelatin as with that prepared from acid-process gelatin (isoelectric point 8.0). However, the rate at a given *p*H, and indeed the character of the development curve, varied markedly with the concentration of oxalate. The dependence of rate upon oxalate concentration proved to be just the opposite from that found in more acid solution. Figure 1 illustrates some typical results. All developing solutions contain 0.01 *M* ferrous salt (added as sulfate) and 0.667 *M* potassium nitrate. The latter was added to minimize the gelatin charge-barrier. The dotted curves represent data obtained at *p*H 6.0; the solid curves, data obtained at *p*H 8.3.

At *p*H 6.0, a decrease in the oxalate concentration (below 0.2 *M*) is accompanied by a decrease in the development rate. Only a very faint image developed after three hours when the solution contained only 0.02 *M* oxalate (data are not shown for this particular solution). The general shape of the development curves, however, was not altered appreciably by the change in oxalate concentration.

At *p*H 8.3, the situation is reversed. The development rate *increases* with decreasing oxalate concentration, and the character of the development curve undergoes a significant change. At a

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[1] T. H. James, *J. Chem. Physics*, **12**, 453 (1944).

[2] T. H. James, *J. Phys. Chem.*, **43**, 701 (1939).

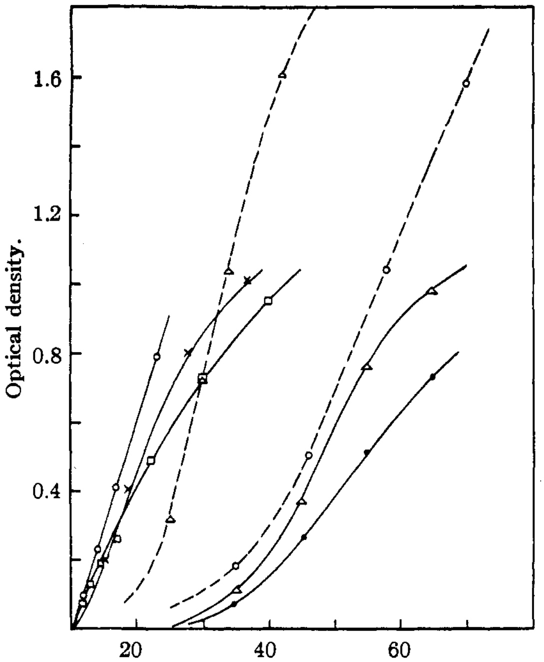

Fig. 1.—Effect of $p$H and oxalate-ion concentration upon the rate of development by iron salt solutions: $FeSO_4$, 0.01 $M$; KBr, 0.0033 $M$; $KNO_3$, 0.667 $M$; log $E$, 1.75; oxalate-ion concentrations: □□, 0.025 $M$; ○○, 0.05 $M$; ××, 0.10 $M$; △△, 0.20 $M$; ●●, 0.60 $M$. The solid lines correspond to $p$H 8.3 (except for the lowest oxalate concentration, where $p$H is 8.1); the dotted lines are for $p$H of 6.0.

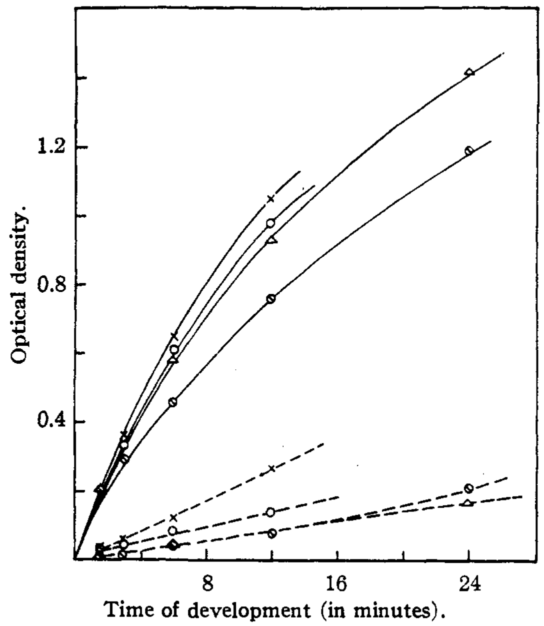

Fig. 2.—Effect of bromide ion on development rate at low oxalate-ion concentration: $K_2C_2O_4$, 0.025 $M$; $FeSO_4$, 0.01 $M$; $p$H = 8.1; log $E$ = 1.75: ××, no added KBr; ○○, 0.0033 $M$ KBr; △△, 0.020 $M$ KBr; ⌀⌀, 0.10 $M$; KBr. Solid lines are image curves; dotted lines are fog.

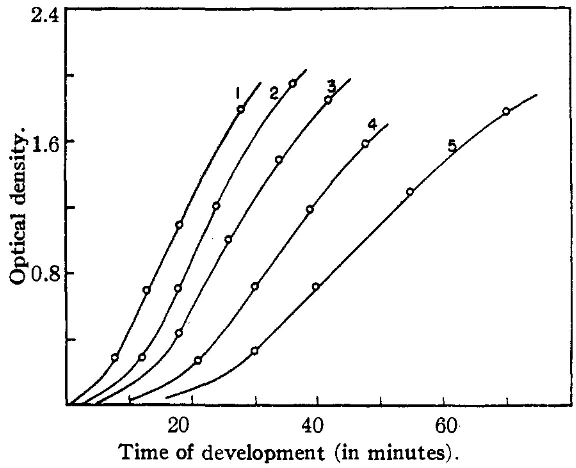

Fig. 3.—Effect of bromide ion on development rate at high oxalate-ion concentration: $K_2C_2O_4$, 0.60 $M$; $FeSO_4$, 0.01 $M$; $p$H, 8.8; log $E$, 1.75: curve 1, no KBr; 2, 0.00033 $M$; 3, 0.0010 $M$; 4, 0.0033 $M$; 5, 0.010 $M$.

sufficiently low oxalate concentration, the induction period disappears. The change in character of the development is shown in other ways. The rate of development at the low oxalate concentration is almost independent of the bromide-ion concentration of the solution, and the fog formation is rather heavy. On the other hand, development in a solution at the same $p$H, but containing 0.2 to 0.6 $M$ oxalate, is quite sensitive to the bromide-ion concentration, and is accompanied by much less fog formation. Figure 2 shows the effect of bromide upon a solution containing 0.025 $M$ oxalate at $p$H 8.1. The solid curves represent image development; the dotted curves, fog formation. If fog corrections are applied to the image data, there is no effect of bromide upon image development, within the limits of experimental error, in the bromide concentration range of 0 to 0.02 $M$. Even at 0.1 $M$ bromide, the effect is small. Figure 3 shows the more normal dependence of development upon bromide-ion concentration in a ferro-oxalate developer. This is obtained even at $p$H as high as 8.8 when the oxalate concentration is 0.60 $M$.

In going from high-oxalate to low-oxalate concentration in alkaline solution, a definite change in the character of development is also indicated by the quantitative change in the dependence upon the amount of light exposure given the photographic material. This is illustrated in Table I. The developing solutions contained 0.01 $M$ ferrous salt and 0.01 $M$ potassium bromide. The data have been corrected for fog. Two sets of data are given, and the times of development for each have been chosen so as to give approximately equal densities at the highest exposure for the two oxalate concentrations.

## Discussion

The concave shape of the initial part of the

TABLE I

DEPENDENCE OF DEVELOPED DENSITY UPON EXPOSURE

$FeSO_4$, 0.01 *M;* KBr, 0.01 *M;* *p*H at 0.6 *M* oxalate, 8.8; *p*H at 0.025 *M* oxalate, 8.1.

| Exposure as log *E* | Density for | | | |
|---|---|---|---|---|
| | 0.6 *M* $K_2C_2O_4$ development. 40 min. | 0.025 *M* 12 min. | 0.6 *M* 55 min. | 0.025 *M* 24 min. |
| 2.05 | 0.90 | 0.90 | 1.46 | 1.45 |
| 1.75 | .72 | .82 | 1.26 | 1.30 |
| 1.45 | .52 | .72 | 1.00 | 1.13 |
| 1.15 | .32 | .58 | 0.70 | 0.95 |
| 0.85 | .13 | .43 | .40 | .74 |
| .55 | .06 | .28 | .20 | .50 |
| .25 | .. | .15 | .09 | .27 |

development curve obtained with slightly acid ferro-oxalate solutions, and particularly the relatively long induction period, are characteristic of development by agents which act in the form of bivalent ions.[2] These characteristics are obtained with alkaline solutions up to at least a *p*H of 9 if the concentration of excess potassium oxalate is sufficiently great. The principal developing agent in such solutions is evidently still the ferro-oxalate ion. At low oxalate concentrations, on the other hand, the alkaline developer gives no induction period, and the development curves have the general shape characteristic of an uncharged developing agent. The lowered susceptibility to bromide, and the decreased dependence upon exposure likewise are to be expected if the active developing agent in this case is not negatively charged.

The alkaline developing solutions containing large excesses of oxalate show the typical deep reddish color of the ferro-oxalate ion. At lower oxalate concentrations, however, the color shifts to a light greenish-blue, and colloidal ferrous hydroxide appears in the solution. Whenever the developer composition was altered in such a way as to eliminate the induction period, whether this was accomplished by decreasing the oxalate concentration or by increasing the *p*H, the solution always contained ferrous hydroxide. The latter may indeed be the principal developing agent in such solutions. Development can be obtained in the complete absence of oxalate by using a solution of ferrous sulfate made slightly alkaline by addition of borax or sodium hydroxide. Development starts rather quickly, but the rate falls off rapidly as ferrous hydroxide coagulates, and only a weak image is obtained.

It is possible that ferrous ion itself is the developing agent in the alkaline solutions containing little or no oxalate. Ferrous sulfate in acid solution does not develop, but Luther[3] has explained this as due to the highly unfavorable equilibrium point in the system: $Fe^{++} + \overset{+}{Ag}\overset{-}{Br} \rightleftarrows Fe^{+++} + Ag + Br^-$. An increase in the *p*H of the solution would favor reduction, since ferric oxide is far less soluble than ferrous hydroxide. However, there is no evidence to show that the reaction rate between ferrous ion and silver bromide would be adequate to explain the present observations. Ammann-Brass obtained development with acid ferrous sulfate solutions when the accumulation of ferric ions was prevented by keeping zinc or iron powder suspended in the solution,[4] but the net rate of development in all his experiments was far smaller than the rates observed in the present work.

If ferrous hydroxide is the active developing agent, the oxalate, when present, facilitates the reaction by aiding in the transfer of ferrous hydroxide to the reaction centers. Some ferro-oxalate ion will exist in equilibrium with the ferrous hyroxide (colloidal). Ferrous hydroxide, freshly formed by hydrolysis of ferro-oxalate ions which have already penetrated into the gelatin layer, will be mainly responsible for the development. Colloidal particles of ferrous hydroxide outside the gelatin layer would not be expected to penetrate as such to the grain surface. In the absence of oxalate, only weak development is obtained because very little ferrous hydroxide reaches the silver bromide grains. Development is confined to grains very near the surface of the gelatin layer. Even in the presence of small amounts of oxalate, development does not penetrate very deeply into the gelatin layer. Even after a strong image is visible from the outer side of the film, scarcely any image is visible from the support side before the unreduced silver halide is dissolved out.

It has been suggested to the writer, by S. E. Sheppard and R. H. Lambert, of these Laboratories, that the active molecular species here may be neither the bivalent $Fe^{++}$ ion, nor the neutral molecule $Fe(OH)_2$, but the intermediate monovalent ion $Fe^+OH$, which is produced as the first stage hydrolytic product according to the reaction[5]

$$Fe^{++} + H_2O \rightleftarrows Fe^+OH + H^+$$

The evidence for this is based on solubility and conductivity data which indicate that the *solution* of ferrous hydroxide is a strong electrolyte, that is, totally dissociated, but that at *p*H $\sim$ 8.0 there are some 200 $Fe^+$ OH ions to 1 $Fe^{++}$ ion.

Uncharged, undissociated ferrous oxalate is another possibility as the real developing agent. However, it is not certain that this species exists in sufficient concentration in solution. Although the conductivity of saturated ferrous oxalate solutions is abnormally low, Scholder[6] has shown that the conductivity data can be explained by the formation of the ferro-oxalate complex, without

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(3) *Cf.* S. E. Sheppard and C. E. K. Mees. "Investigations on the Theory of the Photographic Process," Longmans, Green and Co., London, 1907, p. 65 ff.

(4) H. Ammann-Brass, *Phot. Ind.*, **35**, 827 (1937).

(5) Folke-Lindstrand, Separate, A.-B. Gleerupska Univ.-Bokhandeln, Lund, 1939, 103 pages [*C. A.*, **34**, 3027 (1940)].

(6) R. Scholder, *Ber.*, **60**, 1525 (1927).

assuming a low degree of dissociation of the ferrous oxalate itself.

The low-oxalate, alkaline developers deposit ferric oxide along with the silver during development. If the silver is removed by suitable means, a ferric-oxide image remains behind. If the solution is sufficiently alkaline, ferric oxide is deposited even in the presence of considerable amounts of oxalate. At *p*H 8.7, strong oxide images were obtained even in the presence of 0.2 *M* oxalate, although little ferric oxide was in evidence at 0.6 *M* oxalate.

## Summary

1. The rate of development in a dilute ferro-oxalate developer of low excess oxalate-ion concentration increases with *p*H in the range 8.0 to 8.5. The increase was observed with photographic films made with lime-process gelatin and with acid-process gelatin. The increase was not observed at high excess oxalate-ion concentration, where the development characteristics are those of development by a doubly charged agent.

2. At low excess oxalate-ion concentration and *p*H greater than 8.0, development shows no induction period and very little sensitivity to bromide-ion concentration. The general characteristics are those of development by an uncharged (or possibly a positively charged) agent.

3. It is suggested that ferrous hydroxide (or the $FeOH^+$ ion) is the active developing agent.

ROCHESTER, NEW YORK RECEIVED JULY 27, 1945

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# Rearrangements in Compounds of Carbon, Silicon, Germanium and Tin containing Halogens, Isocyanate and Thiocyanate

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The redistribution reactions, long known qualitatively,[1] were first quantitatively shown to be random by Calingaert and co-workers[2] in certain alkyls, chloroalkyls and ethylene halides. A previous paper[3] demonstrated the same outcome in the silicon chloroisocyanates. Further we have shown in a recent report[4] that the chlorobromides of carbon, silicon, germanium and tin, also the chloroiodides of silicon, all tend toward random distribution. The halides of carbon require a catalyst such as slightly moistened aluminum chloride, while the mixed halides of each succeeding element of Group IVA react with greater speed at distillation temperatures. In these papers[3,4] we have discussed the redistribution reaction from qualitative and quantitative standpoints, and have cited typical papers upon the subject without any effort to make the list complete. Still more recently, Mayo and Dolnick[5] have studied catalyzed rearrangements, at equilibrium, of halogen atoms in dihaloethanes and in bromopropanes.

The purpose of this article is to describe a study from the same standpoint, of a greater variety of Group IVA compounds. These include methane derivatives containing two or three halogen atoms, the recently synthesized trichlorosilicon thiocyanate,[6] germanium chloroisocyanates, and in addition oxidation products of stannous oxide and stannous fluoride.

## Experimental

**Chloroform and Bromoform.**—No previous record of a reaction between these compounds could be found. Under the conditions described below, approximately random distribution was attained, as shown in Table I. The hydrogen showed no perceptible tendency to migrate. To minimize separation of carbon, oxygen was displaced by carbon dioxide. This method is advantageous for preparation of the two intermediate chlorobromides.

Bromoform was prepared by gradual addition of bromine and sodium hydroxide to a water solution of acetone.[7] The crude product was washed, dried with calcium bromide, and purified by distillation with care to collect material boiling from 149 to 150° for use in redistribution studies. Bromoacetone, b. p. 136.5°, was present in traces only. Mixtures of chloroform and bromoform were heated in sealed tubes in presence of potassium chloride and aluminum chloride containing hydrochloric acid produced by partial hydrolysis. The crude product was washed with caustic solution, then with water and centrifuged to help the separation of the layers. After drying with calcium chloride the mixture was analyzed by distillation using the following procedure, typical of all the experiments with carbon and germanium compounds. A liquid mixture of 3–6 ml. was distilled using a column 20 cm. high made of tubing 7 mm. in outside diameter and having a spiral of no. 22 copper wire with 56 turns. Distillation curves of mixtures of *stable* components boiling 30° or more apart always consist of "flats" close to predicted boiling points connected by steep, almost linear sections. Readings of temperature and of volume were made simultaneously; the latter was measured to 0.01 ml. in special tubes of 1–2 ml. capacity graduated to 0.1 ml. These tubes were checked at several points by delivery of mercury from a standardized 0.1 ml. micropipet. Thus the volume of any particular fraction was known within 0.01–0.02 ml., or within 1% of the total volume of the reaction product,

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(1) See, for instance, Besson, *Compt. rend.*, **122**, 814 (1896).

(2) Calingaert and others, THIS JOURNAL, **61**, 2748, 2755, 2758, 3300 (1939); **62**, 1099, 1104 (1940).

(3) Anderson, *ibid.*, **66**, 934 (1944).

(4) Forbes and Anderson, *ibid.*, **66**, 931 (1944).

(5) Mayo and Dolnick, *ibid.*, **66**, 985 (1944).

(6) Anderson, *ibid.*, **67**, 223 (1945).

(7) L. Vanino, "Handbuch der präparativen Chemie," Vol. II, F. Enke, Stuttgart, 1937, p. 15.