Identification of Halogens in Organic Compounds by Means of Paper Chromatography(1)

By Toshio ANDO and Shin-ichi ISHII

(Received November 17, 1951)

In order to identify halogens contained in organic compounds, a usual method of qualitative inorganic analysis has been applied to the solutions obtained by decomposition of the compounds. However, such an analysis is somewhat troublesome and needs a considerable amounts of samples. Lederer(2) has recently described a chromatographic method for the separation of inorganic halides on paper with butanol-ammonia as solvent, but the resolution of chloride and bromide especially was not complete, and the instability of composition of the solvent resulting from vaporization of ammonia was also found undesirable.

Now the present authors have developed a method of identifying halogens of organic substances accurately on paper chromatograms, in which a few drops of Lassaigne's solution obtained by decomposing the compounds in the usual way with sodium were developed favorably with a solvent consisting of butanol-picoline. The spots of chloride, bromide, and iodide were then revealed separately as brown coloration of silver sulfide. A spot of iodide could also be located by a characteristic violet coloration of iodine-starch compound.

Experimental Method

Sample.—0.1 M solutions of sodium chloride. bromide, and iodide in water and in aqueous sodium hydroxide of 0.5, 1.0, 1.5, and 3.0 N in concentration were used at first for the sake of control. Those of sodium cyanide, sodium sulfide, and potassium rhodanate were also used. The organic substances containing halogen which were used were as follows: benzene hexachloride, chloronitrophenol and aniline hydrochloride (both containing Cl and N), dibromocholestanedione,

---

(1) The present paper was read by one of the authors (S. I.) before the 7th Meeting of this Institute (Nov. 9, 1950) and also before the 4th Annual Meeting of the Chemical Society of Japan in Tokyo University held on April 7, 1951.

(2) M. Lederer, *Science*, **110**, 115 (1949).

bromophenol blue and bromothymol blue (Br and S), ammonium bromocamphorsulfonate (Br, N and S), and diiodotyrosine (I and N), and also some combinations of them.

Decomposition of the organic compounds.—A small quantity of organic halogenocompound was fused with 3∼5 parts of metallic sodium, and the mixture was poured into water of 30∼40 times the weight of sodium used. 0.01∼0.005 cc. of the Lassaigne's solution thus prepared was applied to a strip of paper.

Filter paper.—A strip (1.8×22 cm.) of the Toyo filter paper No. 131 was used. The Toyo filter paper No. 2 was found unsuitable for the present purpose, as it always contained a slight quantity of chloride and the chromatogram obtained on it was not so fine as to distinguish the spots clearly.

Development and revelation.—One-dimensional ascending type of development was adopted in a test-tube (2.5×25 cm.) containing solvent in the bottom.

Solvents used were as follows: (a) butanol-picoline-water (1:1:0.8 V/V), (b) butanol-propanol-water (1:1.1:1 V/V), and (c) butanol-$1.5\,N$ aqueous ammonia (5:1 V/V). Temperatures were given respectively in the foot-notes of the table.

After development and drying, the paper was sprayed with $0.2\,N$ aqueous solution of silver nitrate, followed by washing away the excess of silver nitrate twice with $0.1\,N$ nitric acid. Then the paper was either sprayed with $0.2\,N$ solution of sodium sulfide or exposed to the atmosphere of hydrogen sulfide. The spot of halide was revealed as brown coloration of the resulting silver sulfide.

In a case of iodide, the following method was also used and proved more sensitive than the former: after development the paper was sprayed with 3% aqueous hydrogen peroxide and then with 0.2% aqueous solution of starch. A fine bluish violet spot of iodine-starch appeared instantly.

Results and Discussions

RF values of various solutions of inorganic halides, sulfide, and rhodanate when developed with butanol-picoline, butanol-propanol, and butanol-ammonia, and also those of halides obtained from organic compounds containing halogens were summarized in the accompanying table.

Chromatograms of aqueous solutions of inorganic halides.—In aqueous solution of sodium chloride, bromide, or iodide, the butanol-picoline system was found most suit-

Table

RF Values of Several Halides and Salts Dissolved in Water or Alkaline Solutions of Various Concentrations and Developed with Several Solvents(a)

Developing Solvent	Solution of Sample ($0.1\,M$) in	Halide			Other Relating Salt	
		NaCl	NaBr	NaI	Na_2S	KCNS
Butanol-Picoline(b)	Water	0.22 §	0.31	0.59	0.03	0.64
	$0.5\,N$-NaOH	0.19	—	—		
	$1\,N$-NaOH	0.18	0.28	0.56		
	$1.5\,N$-NaOH	0.15	—	—		
	$3\,N$-NaOH	0.10	—	—		
	Decomposition Solutions of Organic Halogenocompounds*	0.19 ±0.02	0.27 ±0.02	0.56 ±0.03		
Butanol-Propanol(c)	Water	0.28	0.32	0.40	0.14	0.48
	$0.5\,N$-NaOH	0.27	—	—		
	$1\,N$-NaOH	0.23	0.26	0.34		
	$1.5\,N$-NaOH	0.21	—	—		
	$3\,N$-NaOH	0.18	—	—		
Butanol-Ammonia(d)	Water	0.05	0.08	0.14	0.00_6	0.20
	$0.5\,N$-NaOH	—	—	—		
	$1\,N$-NaOH	0.05	0.07	0.13_5		
	$1.5\,N$-NaOH	—	—	—		
	$3\,N$-NaOH	—	—	—		

(a) By an ascending method. (b) Butanol-picoline-water (1:1:0.8 V/V); picoline was collected between b. p. 120∼155° of pyridine base. Developing temperature was 5∼10°. (c) Butanol-propanol-water (1:1.1:1 V/V). Temperature was about 25°. (d) Butanol-$1.5\,N$ aqueous ammonia (5:1 V/V). Temperature was about 28°.

* Summarized results were given.

§ KCl and $CaCl_2$ in aqueous solutions gave RF values of 0.22 and 0.23 respectively, while $CuCl_2$ and HCl those of about 0.38 and 0.40 respectively, forming presumably salts with picoline.

able to resolve the halides.(3) It was also found that, with the same solvent, an elevation of temperature caused a tendency of decreasing in R_F values, while a dilution of the solution caused a tendency of increasing in R_F.

Application of 0.005 cc. of 0.1 *M* solution proved most adequate, yet the spot could be detected even with 0.01 *M* solution.

An aqueous solution of the chloride of potassium or calcium was also developed with the same solvent and was found to show the same R_F value for the chloride. That of cupric chloride or hydrogen chloride, in contrast, gave somewhat greater value in R_F, where the halides seemed to move forming salts with picoline (see the foot-note marked with § in the table).

The butanol-propanol system proved also useful as a solvent, although differences among R_F values of the chloride, bromide, and iodide became somewhat smaller, whereas butanol-ammonia gave too small R_F values for all halides and only too small differences among them to distinguish spots clearly. Only in the case of iodide, which often appears as a partly diffused spot on a butanol-picoline chromatogram, development with either one of the other two solvents, if necessary, will be useful.

Influence of alkali on the chromatogram.—As the decomposition solution of organic halogenocompound is alkaline, the influence of alkali on the chromatogram was examined using 0.1 *M* solutions of halides in $0.5\sim3.0\,N$ sodium hydroxide. As shown in the table, an aqueous caustic soda was found to decrease slightly the R_F values of halides with an increase in its concentration. It may, however, be considered that no such remarkable effect as to disturb identification of halides was seen in practice on the R_F values or on the shapes of the spots, so far the concentration of alkali lower than *ca.* 1.5 *N* was used.

Chromatograms of the decomposition solutions of organic substances containing halogens.—According to the directions given before for the decomposition of organic substances, just an alkaline solution of $1\sim1.5\,N$ concentration should be prepared, in which practically no influence on the spots of halides could be observed as described above.

R_F values with butanol-picoline of halides of such solutions obtained from various organic halogenocompounds used alone or in some admixtures, either containing nitrogen and sulfur in addition to halogen or not, were always in good agreement respectively with those obtained in control experiments (see the table), shapes of the spots being also unaffeted. Halogen of organic compound containing one atom at least per molecular weight 1,000 is to be successfully identified by this procedure, taking into account the limit of detection observed before with control test.

When the solution to be tested, if necessary, is applied by the side of or mixed with an authentic specimen of sodium halide in question and developed, the resulting figure will add a more reliable fact. Separation and identification of halogens in organic compounds were thus found satisfactory.

The present method of analysis seems to be applied also to the solution obtained microtechnically by decomposing organic halogenocompound on heating with the mixture of magnesium and anhydrous potassium carbonate (Foulke-Schneider method(4)). But no solvent could yet be found applicable for the solution obtained by the Carius method of decomposition with fuming nitric acid.

Chromatograms of sulfide and rhodanate.—In the case of an organic substance containing nitrogen or sulfur, or both together, there may be produced cyanide or sulfide, or both and sometimes rhodanate in the decomposition solution with sodium. Accordingly, specimens of such salts were also developed.

When revealed in the usual way except washing with water instead of with dilute nitric acid, sodium cyanide showed only a very faint spot near the original point with every solvent used in the experiment. Sodium sulfide gave a spot of low R_F value as shown in the table merely by spraying with aqueous silver nitrate. By the usual method of revelation, on the contrary, potassium rhodanate alone or even in admixture with halides showed a spot located always above that of iodide in case of every solvent, as shown in the last column of the table. In fact, on dealing with the solution from an organic compound containing (besides halogens) both nitrogen and sulfur, such a spot often appeared just at the point accounted above.

It was thus confirmed that these salts gave influence neither upon R_F values nor on shapes of halides existed together.

Summary

Paper chromatograms of sodium halides such

---

(3) It appears that each halide moves mainly in a form of the salt as it was. When developed with butanol-picoline, especially when halides dissolved in water were used, a faint ghost was always found just above each spot of halides, and seemed likely to consist of a salt of picoline with halide ion partly separated.

(4) G. Foulke and F. Schneider, *Ind. Eng. Chem., Anal. Ed.*, **10**, 102 (1938).

as chloride, bromide, and iodide, dissolved in water or in aqueous caustic soda of various concentrations, were studied with butanol-picoline, butanol-propanol, or butanol-ammonia as a developing solvent, in order to identify such halides accurately by their R_F values on chromatograms, and further to apply the result for the identification of halogens contained in organic substances.

The spots of halides after development were revealed by their brown coloration of silver sulfide formed through silver halides. Iodide was better identified by means of a characteristic starch method.

It was found that butanol-picoline was a suitable solvent to separate spots of the three halides completely, and that these suffered little influence on R_F value or on shape by caustic soda contained in solutions so far as its concentration was within *ca.* 1.5 *N*. Sodium cyanide and sulfide, and potassium rhodanate were also chromatographed and it was found that they were located quite separately from halides and did not disturb the identification of the latter.

On chromatographing a few drops of the decomposition solution with sodium (the alkaline concentration being within the limit quoted above) of various organic substances, which, in addition to halogen, may sometimes contain either nitrogen or sulfur, or both together, halogens contained in them were identified quite satisfactorily based on the results obtained above.

The authors wish to express their hearty thanks to the Ministry of Education for the Scientific Research Grant given for this work.

Institute of Science and Technology,
Tokyo University, Komaba-machi,
Meguro-ku, Tokyo