Different strengths of ferric chloride solutions seem to bring no difference in their behavior towards the sulfinic acid solutions.

LAHORE, INDIA

[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORIES, UNIVERSITY OF THE PUNJAB]

A QUICK METHOD FOR ESTIMATION OF HALOGENS IN CERTAIN ORGANIC COMPOUNDS

BY S. KRISHNA AND JOTI SWARUP

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Several methods are available for quantitative determination of halogens in organic compounds and these are employed when total halogen is to be estimated. But in compounds where two types of halogen atoms are present (as in chlorobenzene sulfonyl bromide) and the amount and proportion of each of these has to be determined some modification of the above methods has to be employed. When the two halogen atoms behave differently such quantitative determination becomes a comparatively easy matter. For example, in chlorobenzene sulfonyl bromide bromine is much more labile than chlorine and hence reacts differently with certain reagents. Based on this principle, Hirst and Macbeth[1] have developed a method of estimating labile halogen on reaction with hydrazine hydrate by measuring the volume of nitrogen evolved according to the equation

$$RSO_2NCl_2 + NH_2NH_2 \longrightarrow RSO_2NH_2 + N_2 + HCl$$

Sometimes an organic compound has to be prepared by a process that involves several stages of intermediate compounds and these intermediate compounds have to be analyzed in order to find their purity. The case in view is the preparation of chloronitrobenzene sulfinic acid ($Cl:NO_2:SO_2H$ 1:4:2) from the corresponding sulfonic acid by reduction of sulfonic chloride. The sulfonic chloride has to be analyzed every time it is prepared. The usual methods involve great length of time, and therefore need was felt for some rapid method of estimation of one of the elements in such compounds. The present communication describes a method of estimating quickly labile halogens in certain organic compounds.

Krishna and Das[2] have shown that Baumann and Kux's method[3] can be employed for the estimation of sulfinic group. It is assumed that sulfonic acids would also react in the same manner as sulfinic acids toward a mixture of potassium iodide and potassium iodate. Thus it becomes possible to estimate sulfonic chlorides, since these on hydrolysis give

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[1] Hirst and Macbeth, *J. Chem. Soc.*, **121,** 904 (1922).

[2] Krishna and Das, *J. Ind. C. S.*, **1927**, 367.

[3] Baumann and Kux, *Z. anal. Chem.*, **32**, 129 (1893).

sulfonic and hydrochloric acids. In the case of *p*-toluene sulfonic chloride, for instance, the reaction proceeds according to the following equations

$$\begin{aligned} 6CH_3C_6H_4SO_2Cl + 6H_2O &= 6CH_3C_6H_4SO_3H + 6HCl \\ 6CH_3C_6H_4SO_3H + 5KI + KIO_3 &= 6CH_3C_6H_4SO_3K + 3H_2O + 3I_2 \\ 6HCl + 5KI + KIO_3 &= 6KCl + 3H_2O + 3I_2 \\ 6I_2 + 12KOH + 6H_2O_2 &= 12KI + 12H_2O + 6O_2 \end{aligned}$$

so that the chlorine present in the compound is equivalent to one-half of the oxygen that is liberated. It is well known that such substances as sulfonyl chloride, acid chlorides, picryl chloride, etc., are characterized by the facility with which they undergo hydrolysis. In compounds like chlorobenzene sulfonyl bromide, therefore, bromine which is in labile condition can easily be removed as hydrobromic acid and estimated as shown above.

Such compounds as have a labile halogen and a nitro group (as *o*-chloronitrobenzene, picryl chloride, etc.) give higher values than are demanded by theory. This may be due to the fact that the nitrophenols which are liberated on hydrolysis behave as weak acids and therefore react to some extent with potassium iodide and iodate solutions. It has been shown by Conant and Kirner[4] that the halogen atom in ACH_2Cl is more reactive than ACl, where A is a phenyl group. An attempt was therefore made to estimate halogen in benzyl chloride by the present method but it was found that only about 90% of the halogen could thus be estimated. Benzal chloride, however, gave satisfactory results according to the equations

$$\begin{aligned} 3C_6H_5CHCl_2 + 5KI + KIO_3 &= 3C_6H_5CHO + 6KCl + 3I_2 \\ 3I_2 + 3H_2O_2 + 6KOH &= 6KI + 3H_2O + 3O_2 \end{aligned}$$

Halogen substituted fatty acids as, for example, monochloro-acetic, monobromo-acetic, ethyl chloroformate, etc., gave results that were in accordance with the usual Kux's equation. Chloral hydrate gave higher results and this may be due to the fact that the aldehyde group present in chloral hydrate is partly oxidized to carboxyl group by hydrogen peroxide and the acid thus formed reacts with iodide and iodate, giving higher values. Substances like dichloro-ethylene, however, react in the usual manner, liberating an equal volume of oxygen.

The following factors are essential to the success of the experiment.

1. The approximate adjustment of the proportions in which the reagents are mixed. Three g. of potassium iodide, 0.3 g. of potassium iodate (acid free), 2 cc. of 3% hydrogen peroxide and 4 cc. of carbonate-free potassium hydroxide (1:1) gave the best results.

2. Adjustment of the various conditions at the time of mixing the potassium iodide and the potassium iodate with the organic substance. In some cases the compound had to be boiled with water before the addition

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[4] Conant and Kirner, THIS JOURNAL, **46**, 232 (1924).

of the above reagents at room temperature, whilst in others the addition of the reagents had to be carried out in ice-cold solutions. The various conditions are mentioned in the experimental portion of the work.

Experimental

The apparatus as described by Baumann and Kux[3] was employed and adjusted for measurements as described in "The Methods of Quantitative Organic Analysis."[5] A known weight of the labile halogen compound (about 0.15 g.) was introduced into the outer vessel, A, with a solution of 3 g. of potassium iodide and 0.3 g. of potassium iodate. Into the inner vessel, B, was taken a freshly made and cooled mixture of 2 cc. of 3% hydrogen peroxide and 4 cc. of potassium hydroxide.

The sulfonic iodide, bromides and chlorides used in this work were prepared according to Otto and Tröger.[6] The results for *p*-toluene

TABLE I

ESTIMATION OF IODINE IN *p*-TOLUENE SULFONIC IODIDE

Time Taken to Complete the Reaction, Thirty Minutes

I Experiment no.	II Weight of sulfinic iodide taken, g.	III Wt. of oxygen, g.	IV Wt. of oxygen equivalent to iodine present, g.	Corresponding wt. of iodine, g.	Iodine found, %	Iodine calcd., %	Percentage error
1	0.1263	0.0144	0.0072	0.0569	45.06	45.01	+0.05
2	.1317	.0149	.0075	.0591	44.87	45.01	− .14
3	.1867	.0211	.0105	.0836	44.8	45.01	− .21
4	.1993	.0226	.0113	.0898	45.06	45.01	+ .05

TABLE II

ESTIMATION OF HALOGENS IN VARIOUS SULFONIC HALIDES

	Sulfonic halide	Halogen calcd., %	Halogen found, %	Error, %	Time taken to complete reaction, hours[a]
1	*p*-Toluene sulfonic bromide	34.02	34.00	−0.02	1
2	*p*-Toluene sulfonic chloride	18.64	18.63	− .01	3
3	Chlorobenzene sulfonic bromide (bromine)	31.28	31.32	+ .04	1
4	Chlorobenzene sulfonic iodide (iodine)	41.96	41.86	− .10	0.5
5	Chlorobenzene sulfonic chloride (active chlorine)	16.82	16.79	− .03	3
6	*p*-Methoxytoluene sulfonic bromide	30.17	30.14	− .03	1.5
7	*p*-Methoxytoluene sulfonic iodide	40.69	40.64	− .05	0.75
8	*p*-Methoxytoluene sulfonic chloride	16.11	16.09	− .02	3.5
9	Sulfonic chloride of benzoic acid	16.11	16.08	− .03	3.5

[a] The time taken to complete the reaction which is given in the last column of Tables II, III and IV is that at the end of which no more oxygen was evolved on longer standing. In cases where no time is given, the volume of oxygen did not become stationary even after a long time.

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[5] P. C. R. Kingscott and R. S. G. Knight, Longmans, Green and Co., London, **1914,** p. 74.

[6] Otto and Tröger, *Ber.*, **24,** 478–488 (1891).

sulfonic iodide are given in Table I as a typical case. The mean results with other sulfonic halides are recorded in Table II.

TABLE III

ESTIMATION OF HALOGENS IN ACID CHLORIDES

	Name of substance	Halogen calcd., %	Halogen found, %	Error, %	Time taken to complete reaction, hours
1	Benzoyl chloride	25.26	25.22	−0.04	0.75
2	Acetyl chloride	45.22	45.05	− .17	.5
3	Phthalyl chloride	34.97	34.93	− .04	2
4	*p*-Nitrobenzoyl chloride	19.13	20.98	+1.85	..
5	*o*-Nitrobenzoyl chloride	19.13	21.18	+2.05	..

TABLE IV

ESTIMATION OF HALOGENS IN OTHER HALOGEN COMPOUNDS

	Name of substance	Halogen calcd., %	Halogen found, %	Error, %	Time taken to complete reaction, hours
1	Benzyl chloride	28.06	25.30	−2.76	4
2	Benzal chloride	44.10	43.99	−0.11	0.75
3	Monochloro-acetic acid	37.56	37.47	− .09	3
4	Monobromo-acetic acid	57.55	57.46	− .09	2.5
5	Ethyl chloroformate	32.71	32.75	+ .04	3
6	Chloral hydrate	64.35	66.87	+2.52	..
7	Dichloro-ethylene	73.19	73.12	+0.07	3
8	Picryl chloride	14.34	28.89	+14.55	..
9	*o*-Chloronitrobenzene	22.54	25.33	+2.79	..

Summary

Kux's iodine method for the estimation of carboxyl group has been successfully used for the estimation of labile halogens in certain halogenated organic compounds. It is found to be inapplicable to those compounds where a nitro group or an aldehyde group is present in the compound. Benzyl chloride and chloral hydrate give unsatisfactory results.

The method can also be used for the estimation of one of the halogen atoms in compounds that contain two different halogen atoms, one of which is present in the labile state, as in chlorobenzene sulfonic iodide.

LAHORE, INDIA