by a new term called the critical oxidation potential. This is the potential of some oxidizing solution which will cause a certain small amount of the amine or phenol to become oxidized in five minutes when equivalent amounts of the sample and of the oxidizing agent are employed. This value, which may be determined with reasonable accuracy, represents the potential at which the velocity of oxidation becomes vanishingly small, and hence the result is influenced by the reaction rate to an extent which is insignificant. This has been demonstrated experimentally, for the critical oxidation potential bears a definite relationship to the normal potential, and it is influenced no more by temperature changes than is the latter quantity.

The critical oxidation potentials of over seventy compounds have been determined and many relationships, conclusions and deductions have been pointed out in discussing the results.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

SOME ERRORS IN ANALYTICAL BROMINATION. THERMAL CLEAVAGE OF HYDROGEN BROMIDE FROM BROMINATED SUBSTANCES. A NEW PROCEDURE FOR DETERMINATION OF ORGANIC UNSATURATION[1]

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I. Introduction

Halogenation methods for the determination of organic unsaturation are in general referable to three types, based upon the nature of the agent and the medium: (1) iodine–halide methods, such as those of Hübl, Wijs and Hanus, conducted in non-aqueous solvents;[2] (2) bromination in non-aqueous solvent, especially carbon tetrachloride, the best-known method being that of Schweitzer–Lungwitz–McIlhiney;[3] (3) the bromide–bromate method, conducted in the presence of water, and due to Koppeschaar.[4]

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[1] Thesis presented by Howard M. Buckwalter to the Graduate School of the University of Pennsylvania in partial satisfaction of the requirements for the degree of Doctor of Philosophy.

[2] Hübl, *Dingler's Polytech. J.*, **253**, 281 (1884); *J. Soc. Chem. Ind.*, **3**, 641 (1884); Ingle, *ibid.*, **21**, 587 (1902); **23**, 422 (1904); Wijs, *Ber.*, **31**, 750 (1898); Marshall, *J. Soc. Chem. Ind.*, **19**, 213 (1900); Kemp, *Ind. Eng. Chem.*, **19**, 531 (1927); Hanus, *Z. Nahr. Genussm.*, **4**, 913 (1901).

[3] Schweitzer and Lungwitz, *J. Soc. Chem. Ind.*, **14**, 130 (1895); McIlhiney, THIS JOURNAL, **16**, 275 (1894); **21**, 1084 (1899); **24**, 1103 (1902).

[4] Koppeschaar, *Z. anal. Chem.*, **15**, 233 (1876).

The last method has been applied to determine unsaturation,[5] but is most useful in the analysis of phenols and aromatic amines.[6]

A useful classification of the non-aqueous methods differentiates those which permit determination of only the total halogen consumed and those which attempt its distribution into halogen used in addition and that used in substitution. Methods of the first kind (Hübl, Wijs, Hanus) employ what are probably less severe halogenating agents, especially iodine halides, and short periods of halogenation when possible, with exclusion of light, to minimize substitution. They are satisfactory only when complete addition, without substitution, can be effected under these conditions,[7] and may not be applicable to compounds whose unsaturation is for any reason less accessible to halogenation.[8] In methods of the second type the extent of substitution is determined by the device of titrating the hydrogen bromide of substitution.[9]

The sample, in an iodine flask, is treated with a measured excess of a standard solution of bromine (or iodine chloride or bromide) in carbon tetrachloride. After a suitable interval (thirty minutes to eighteen hours) potassium iodide solution is introduced, and the liberated iodine, equivalent to the excess halogen, is titrated with thiosulfate. Potassium iodate solution is then introduced, and the liberated iodine, equivalent to the hydrogen bromide of substitution, is titrated. The total halogen consumed, less twice that represented by the second titration, is that taken up by addition.

The only really satisfactory solvent appears to be carbon tetrachloride, in which halogenation is irreversible,[10] and which when properly purified is neutral and not attacked by the dissolved halogen.[11] The greater effectiveness of iodine halide in carbon tetrachloride solution (method of Marshall[2]), compared with that of the solution in acetic acid, was shown by Böeseken and Gelber.[8] Bromine in carbon tetrachloride appears to be equally vigorous. The fact that the increased saturating power of

[5] Klimont, *Pharm. Post.*, **44**, 587 (1911); *Chemical Abstracts*, **6**, 1203 (1912); Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

[6] Callin and Henderson, *J. Soc. Chem. Ind.*, **41**, 161 (1922); Day and Taggart, *Ind. Eng. Chem.*, **20**, 545 (1928).

[7] The Wijs method meets these requirements best for the usual fats and oils: "Report of the A. C. S. Committee on Analysis of Fats and Oils," *Ind. Eng. Chem.*, **18**, 1349, 1354 (1926). To avoid substitution in the analysis of the rubber hydrocarbon, however, Kemp [*ibid.*, **19**, 531 (1927)] found it necessary to operate with the Wijs reagent at 0°.

[8] Böeseken and Gelber, *Rec. trav. chim.*, **46**, 158 (1927).

[9] Allen, "Commercial Organic Analysis," 2d. ed., Vol. II, p. 383; McIlhiney, and Schweitzer and Lungwitz, Ref. 3.

[10] In dissociating solvents, including acetic acid, Böeseken and Gelber (Ref. 8) found addition of iodine chloride to be reversible, especially in the neighborhood of negative groups.

[11] Bromine dissolved in chloroform, ethylene bromide or in acetylene tetrabromide generates hydrogen bromide so rapidly that such a reagent cannot be used satisfactorily as a standard solution.

these reagents is accompanied by an increased ability to cause substitution appears to be not a drawback, since the extent of the substitution can be determined.

Both addition and substitution of halogen are influenced, and in ways not always known or predictable, by a variety of factors, including not only time, temperature and quantity and concentration of halogen, but also identity of solvent, condition in which halogen is present, proximity (to the unsaturated condition) of strongly polar radicals or other structural influences, and presence of substances which may operate catalytically. Addition of bromine to unsaturated acids in carbon tetrachloride, according to Williams and James,[12] is catalyzed by traces of hydrogen bromide or water. Davis[13] found light, low temperature and moisture to favor addition of bromine to olefins in carbon tetrachloride. Addition of bromine is retarded by proximity of negative groups,[14] though this influence is not always consistently shown.[15] Difficulty may also be encountered in halogenation of conjugate systems whose saturation is only partial.

Even if it is assumed that addition is initially complete, there are still to be considered several secondary sources of error in methods such as those of Marshall and McIlhiney, due to the reagents added to perform the titrations of the analysis. Several workers[16] have observed replacement of chlorine or bromine by iodine in contact with alkali iodide, in certain cases with subsequent cleavage of iodine to restore the original unsaturation, this effect being favored by negative groups (*e. g.*, —COOH, —$COCH_3$, —COOR, —C_6H_5). Contact of the halogenated sample with water, if followed by hydrolysis, will cause low results by methods in which the HX of substitution is determined.[17] Böeseken and Gelber[8] found that after addition of iodine chloride to certain α,β-unsaturated acids, reversible cleavage of hydrogen chloride became measurable in contact with water, the α-iodo-β-lactone being formed. In the analysis of unsaturated esters, partial ester hydrolysis, promoted by the HX of substitution, would liberate acid which might interfere as indicated below. The presence of water further admits possibility of oxidation by HOX.[18]

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[12] Williams and James, *J. Chem. Soc.*, 343 (1928).

[13] Davis, THIS JOURNAL, **50**, 2769 (1928).

[14] Bauer, *Ber.*, **37**, 3317 (1904); **40**, 918 (1907); **44**, 2691 (1911); Reich, van Wijck and Waelle, *Helv. Chim. Acta*, **4**, 242 (1921); Sudborough and Thomas, *J. Chem. Soc.*, **97**, 715 (1910).

[15] Biltz, *Ann.*, **296**, 231, 263 (1897).

[16] Finkelstein, *Ber.*, **43**, 1530 (1910); Biilmann, *Rec. trav. chim.*, **36**, 313 (1916); van Duin, *ibid.*, **45**, 345 (1926); Böeseken and Gelber, Ref. 8; Dillon, Young and Lucas, THIS JOURNAL, **52**, 956 (1930).

[17] Ingle, *J. Soc. Chem. Ind.*, **21**, 587 (1902); **23**, 422 (1904); Johansen, *J. Ind. Eng. Chem.*, **14**, 288 (1922).

[18] Kolthoff, "Volumetric Analysis," John Wiley and Sons, Inc., New York, **1928**, Vol. I, p. 198.

A third source of error is the presence of an acidic function in the substance analyzed. Such acidity would in general be increased by halogenation, and would affect the results to whatever extent the halogenated sample is able to disengage iodine from iodide–iodate solution. Other errors include possible oxidation by iodate, rupture of a chain or bridge followed by additive halogenation of the nascent free ends, and finally the formation of perhalides.[19]

A hitherto unexplained feature of the McIlhiney or Marshall method is that with certain substances the calculated addition values are *negative, i. e.*, the HX found, when multiplied by 2, indicates the halogen consumed in "substitution"[21] to be more than the total halogen brought into reaction. While in some cases negative error is undoubtedly due to incomplete addition, this cannot safely be assumed from the fact that the calculated addition value is low (unless the total consumption of halogen is also low), for the reason that errors due to certain of the secondary interferences mentioned above would also cause low results even when addition was initially strictly quantitative. With existing procedures it is often impossible to determine whether an error is due to unsuccessful halogenation or to secondary reactions during the titrations. Since the latter are caused by contact of the halogenated sample with water, iodide and iodate, it was concluded that a satisfactory study of analytical halogenation could best be made if such contact were avoided. To this end there was developed the aeration procedure for bromination, now to be described.

II. Aeration Method for Determination of Unsaturation by Bromination

Bromination by a solution of bromine in carbon tetrachloride was effected in an evolution apparatus (Fig. 2) at a suitable temperature, and the excess bromine and the hydrogen bromide produced were removed in a current of dry nitrogen, absorbed in potassium iodide solution, and determined as usual. Except in the case of very volatile substances this procedure avoided contact of the halogenated sample with water, iodide and iodate. In experimental trials of the new procedure, brominations were conducted at 75°, at 20–25° and at 0°. About forty organic substances of various kinds, both unsaturated and saturated, were examined. Comparative analyses were in all cases made by the method of McIlhiney, the bromination period being arbitrarily set at the maximum (eighteen hours).

Apparatus and Reagents

The apparatus consisted of an all-glass evolution flask with a trapped receiver (Fig. 2). For the aeration, nitrogen from a cylinder was passed through Drechsel bottles charged with (1) alkaline pyrogallol, (2) concd. sulfuric acid and (3) granular calcium chloride.

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[19] Kolthoff, Ref. 18, p. 200.

The bromine solution was about 0.28 *N*, containing 7 cc. of bromine per liter of carbon tetrachloride. The best procurable carbon tetrachloride may absorb some bromine and form some hydrogen bromide. It was therefore refluxed for several hours with bromine, cooled, and washed with sodium carbonate solution, dried well over calcium chloride, and distilled through a 5-stage Snyder column, the first and last portions being rejected. It appears that the drying must be thorough, as the presence of moisture was perhaps the cause of subsequent formation of hydrogen bromide in some solutions.

The bromine solution was measured with a 25-cc. Lowy automatic pipet, filled by pressure as suggested in Fig. 1 to avoid the inconvenience and the small loss of bromine involved in filling the pipet by suction.

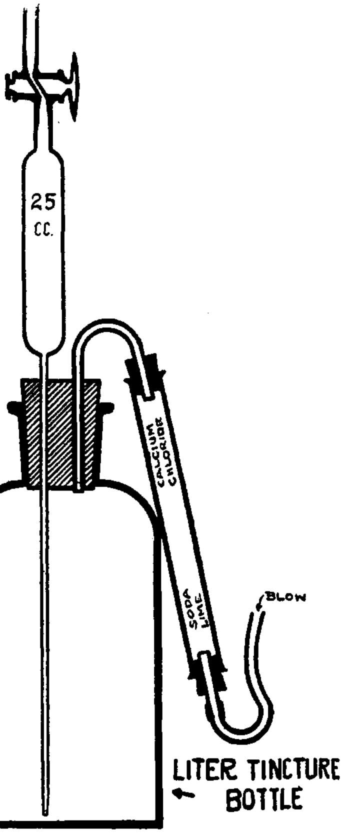

Fig. 1.

To standardize the bromine solution, 25 cc. was pipetted into 150 cc. of 15% potassium iodide solution in a 500-cc. iodine flask, and the iodine was titrated with 0.2 *N* thiosulfate, 5 cc. of 0.5% soluble starch indicator being added near the end-point. There was added 10 cc. of 2% potassium iodate solution, and any iodine liberated was titrated. The liquid was shaken vigorously in the stoppered flask near the end of each titration to extract iodine completely from the carbon tetrachloride layer. The second (acid) titration was generally small and sometimes zero.

The 0.2 *N* sodium thiosulfate was prepared in the usual way, and was standardized against potassium iodate.[20]

Procedure.—Receiver A was charged with 100 cc. of 15% potassium iodide solution, and trap B with 10 cc. of the same, together with about 0.5 cc. of the standard thiosulfate solution, the last being accurately measured from a buret (and its volume finally added to the titration of excess bromine). The sample, in a small glass cup if non-volatile, or in a thin glass bulb or from a Lunge weighing-pipet if a volatile liquid, was introduced into the bromination flask C, and dissolved in 5 cc. of pure carbon tetrachloride. The apparatus was assembled and 25 cc. of the bromine solution introduced by means of the automatic pipet, the tip of which was thrust well into the constriction of D. A gentle suction applied at the trap quickly drew the solution into the flask without loss of bromine. A slow stream of nitrogen (about 20 bubbles per minute) was passed during the ensuing bromination period, at the end of which the flow of gas was increased to about 150–200 bubbles per minute in order to transfer excess bromine, and hydrogen bromide of reaction, as rapidly as possible into the receiver. Repeated blank trials had shown that this operation involved no loss of bromine. The time required for aeration at room temperature was about three and one-half hours.

For bromination at 75° the flask C was immersed, almost to the level of the liquid

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[20] McNabb and Wagner, *Ind. Eng. Chem., Anal. Ed.*, **1**, 32 (1929).

within, in a water-bath at that temperature. During the aeration, which at 75° required only about thirty minutes, carbon tetrachloride was added at intervals to replace that which distilled.

For bromination at 0° the flask C was surrounded by ice, the bromine solution introduced and chilled (with the apparatus assembled), and the sample, in a cup or bulb, introduced into D and washed into the flask with chilled carbon tetrachloride (the bulb being first broken with a glass rod). The aeration at 0° required about six hours.

When the aeration was complete, the apparatus was disconnected at E, the contents of the trap transferred to the main receiver, and the excess bromine and the hydrogen bromide of reaction determined as in the standardization. To calculate, the acid titration, less that of the standardization, was multiplied by 2 and subtracted from the volume of thiosulfate equivalent to the total bromine brought into reaction.

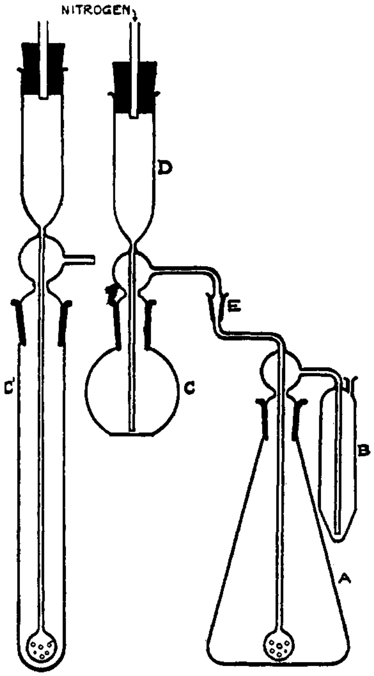

Fig. 2.—A, Receiver, 500-cc. cap.; B, trap, 25-cc. cap.; C, bromination flask, 100-cc. cap.; C', modified form of C; D, funnel; E, ground joint.

Comparative Results by the Aeration Procedure and by McIlhiney's Method.—Results of comparative trials by the two procedures are grouped below according to the general types of compounds examined, or according to the point to be tested. The tables give total atoms of bromine consumed, atoms of bromine used in "substitution,"[21] atoms of bromine added, and percentage of bromine added, *i. e.*, the bromine number. Check analyses by McIlhiney's method represent duplicates run not in the same series but on different days.

1. Determination of Unsaturation of Some Hydrocarbons.—Results for a number of unsaturated hydrocarbons of several types are given in Table I.

Comments.—A distinct temperature effect is shown for cyclohexene, phenanthrene, indene and especially for retene. The case of pinene, for which both methods yielded values converging upon three atoms of bromine added, recalls similar results obtained by Ingle[1] and by Klimont,[4] and also by Wallach.[22] The facts appear to suggest rupture of the isopropyl bridge.

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[21] As this word is used here and elsewhere in this paper when enclosed in quotation marks, it refers to the apparent substitution indicated by analysis. This is calculated from the hydrogen bromide liberated, whatever its source. When the hydrogen bromide found is believed to include that actually due to substitution and some due also te secondary cleavage of hydrogen bromide during the bromination, the process will be termed "substitution."

[22] Wallach, *Ann.*, **264**, 3 (1891).

TABLE I

UNSATURATED HYDROCARBONS

Compound	Method,[a]	Temp., °C.	Time, hrs.[b]	Atoms of bromine Total	Subst.	Added	% Br added	Br no. theory
Octylene	A	60	$^3/_4 + 1$	2.27	0.15	1.98	140.9	142.5
B. p. 123.3°		20	$1 + 4$	2.13	.07	1.98	141.2	
	B	Lab.	18	2.72	.42	1.87	133.5	
		Lab.	18	2.65	.36	1.93	137.2	
Cyclohexene	A	75	$1 + ^1/_2$	2.12	.17	1.77	172.7	194.7
B. p. 82.0°		75	$2 + ^1/_2$	1.99	.11	1.77	172.7	
		20	$^1/_2 + 5$	2.04	.07	1.90	185.2	
		0	$1 + 8$	1.99	.03	1.93	187.6	
	B	Lab.	18	2.15	.19	1.78	173.3	
		Lab.	18	2.08	.12	1.85	180.1	
Limonene	A	75	$1 + ^1/_2$	5.55	.72	4.10	240.4	234.7
B. p. 176.6°		75	$1 + ^1/_2$	4.88	.39	4.11	241.0	
	B	Lab.	18	4.60	.31	3.98	233.6	
		Lab.	18	4.68	.35	3.97	233.1	
Styrene	A	75	$4 + ^1/_2$	2.04	.00	2.04	157.0	153.5
B. p. 146.0°	B	Lab.	18	1.96	.02	1.92	147.4	
		Lab.	18	2.07	.02	2.03	155.9	
Stilbene	A	75	$1 + ^1/_2$	2.01	.00	2.01	89.2	88.7
M. p. 124.0°		75	$1 + ^1/_2$	2.00	.00	2.00	88.7	
		75	$1 + ^1/_2$	2.00	.00	2.00	88.7	
	B	Lab.	18	2.02	.02	2.00	88.7	
		Lab.	18			2.02	89.7	
						2.00	88.7	
Phenanthrene	A	20	$^1/_2 + 6$	2.55	.44	1.68	75.2	89.7
M. p. 99.7°		0	$3 + 7$	2.88	.43	2.02	90.8	
	B	Lab.	18	3.31	.79	1.73	77.6	
		Lab.	18	2.79	.47	1.85	82.9	
Retene	A	75	$1 + ^1/_2$	7.14	3.73	−0.34	−11.8	68.2
M. p. 97.5°		0	$3 + 7$	5.75	1.89	1.97	+67.0	
	B	Lab.	18	6.25	2.23	1.79	61.1	
		Lab.	18	8.00	3.19	1.62	55.3	
Indene	A	75	$1 + ^1/_2$	4.13	1.21	1.69	116.5	137.7
B. p. 182.8°		25	$0 + 5$	2.17	0.17	1.82	125.1	
		0	$2 + 5$	2.26	.22	1.81	124.4	
		0	$^1/_2 + 7$	2.32	.21	1.89	129.9	
	B	Lab.	18	3.91	1.07	1.76	121.3	
		Lab.	18	4.29	1.26	1.75	120.6	
Pinene	A	75	$1.5 + ^1/_2$	4.85	1.09	2.67	156.5	117.4
B. p. 158.8°		25	$13 + 3$	4.65	0.89	2.86	167.6	
		0	$^1/_2 + 7$	4.46	.65	3.16	185.4	
	B	Lab.	18	4.55	.83	2.88	169.3	
		Lab.	18	4.80	.91	2.98	174.9	
		Lab.	18	4.29	.63	3.00	176.3	

[a] A, Aeration method; B, McIlhiney's method.

[b] First figure indicates time of bromination and second figure time of aeration.

Table II records results obtained with several technical hydrocarbon mixtures obtained from petroleum.[23]

TABLE II

PETROLEUM PRODUCTS

For convenience in comparison, the bromine values obtained are all reported as equivalent iodine values.

Sample	Method	Temp., °C.	Time, hrs.	Equiv. % iodine			Refinery lab. results Method of Johansen[16]	
				Total	Subst.	Added	% I Subst.	% I added
Lubricating oil, heavy	A	75	1 + 1/2	67.8	38.3	−8.2	10.9	−1.5
		75	2 + 1/2	55.1	19.1	−5.5		
		23	1 + 3	33.6	16.4	+0.9		
		0	1 + 7	27.2	12.5	+2.2		
	B	Lab.	18	63.8	35.3	−6.8		
		Lab.	18	44.2	23.2	−1.7		
		Lab.	18	45.4	23.5	−1.8		
Transformer oil	A	75	1 + 1/2	62.5	34.6	−6.8	8.3	−0.05
		25	1 + 3	21.0	10.5	−0.1		
		0	1 + 7	15.0	7.1	+0.9		
	B	Lab.	18	64.8	35.1	−5.1		
		Lab.	18	60.0	32.2	−4.4		
Cracked gasoline	A[a]	60	1 + 1/2	118.2	43.4	31.3	23.5	32.8
		20	1 + 8	84.8	25.1	34.7		
		0	1 + 6	67.3	14.7	37.8		
	B	Lab.	18	144.8	53.2	38.4		
		Lab.	18	154.0	58.4	37.3		

[a] Sample passed into receiver on aeration.

2. **Determination of Unsaturation of Some Compounds with Acidic Character.**—Since an iodide–iodate solution is sensitive to acids generally, the effect of an acidic function in the substance analyzed, as was mentioned in the introduction, is to increase the acid titration (after addition of iodate), and to decrease the addition value by double this error. In some cases such acidic function will register quantitatively its acidity, for which deduction can be made in the calculation. If the acidity, however, is of a low order it will introduce an indeterminate error, such irregularity being sometimes suggested by an unusually marked impermanence of the second end-point. Since the causes for error in the bromination of acidic substances are, in general, operative only in the presence of water, etc., such substances are well adapted to test the predictable advantages of the aeration procedure over that of McIlhiney. Results for some unsaturated compounds with acidic function are listed in Table III.

Comments.—The resistance of crotonic acid to halogenation is shown by the ineffectiveness of bromination at room temperature. In McIlhiney's

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[23] Analyzed specimens kindly furnished by the Atlantic Refining Company of Philadelphia, through Dr. J. B. Hill and Mr. E. H. Johansen.

TABLE III

COMPOUNDS WITH ACIDIC FUNCTION

Compound	Method	Temp., °C.	Time, hrs.	Atoms of bromine Total	Atoms of bromine Subst.	Atoms of bromine Added	% Br added	Br no., theory
Crotonic acid	A	75	$1 + {}^1/_2$	2.06	0.05	1.96	182.3	185.7
M. p. 71.8°		75	$1 + {}^1/_2$	2.07	.03	2.01	187.0	
		20	16 + 3	0.31	.00	0.31	22.6	
	B	Lab.	18	.49	.0	.49	45.6	
		Lab.	18	.58	.0	.58	54.2	
Undecylenic acid	A	60	$1 + {}^1/_2$	2.04	.12	1.80	78.1	86.8
M. p. 21–22°		22	1 + 2	1.99	.09	1.80	78.2	
		0	1 + 7	1.89	.05	1.79	77.5	
	B	Lab.	18	2.23	.28	1.67	72.4	
		Lab.	18	2.13	.19	1.75	76.1	
Oleic acid,	A	20	1 + 4	1.99	.11	1.79	50.5	56.6
commercial		0	1 + 8	1.89	.05	1.79	50.7	
	B	Lab.	18	2.19	.24	1.70	48.2	
		Lab.	18	2.19	.23	1.73	48.8	
Fumaric acid	A	75	1 + 2	nil				
	B	Lab.	18	nil				
Maleic acid	A	75	1 + 2	nil				
	B	Lab.	18	nil				
Erucic acid	A	70	$1 + {}^1/_2$	2.56	.51	1.54	36.3	47.2
M. p. 31–32°		70	0 + 1	2.45	.38	1.70	40.1	
		20	15 + 3	2.50	.40	2.10	49.6	
	B	Lab.	18	3.03	.70	1.64	38.7	
		Lab.	18	2.37	.33	1.72	40.6	
Cinnamic acid	A	75	$1 + {}^1/_2$	2.02	.00	2.02	109.1	107.9
M. p. 133°		75	$1 + {}^1/_2$	2.02	.00	2.02	109.2	
	B	Lab.	18	2.00	1.09	−0.19	− 9.9	
		Lab.	18	1.99	0.97	+ .05	+ 2.5	
Abietic acid	A	75	$2 + {}^1/_2$	10.1	6.70	−3.34	−88.1	52.9[a]
M. p. 155°		75	$1 + {}^1/_2$	10.37	6.03	−1.69	−44.8	
From Florida		75	$0 + {}^1/_2$	7.34	3.81	−0.30	− 7.8	
winter rosin		0	0 + 7	4.98	1.65	1.68	+44.3	
		0	1.5 + 8	6.06	1.87	2.33	+61.6	
		0	1 + 7	6.96	2.48	1.99	+52.5	
	B	Lab.	18	10.87	6.56	−2.24	−59.4	
		Lab.	18	9.72	5.37	−1.02	−27.1	
				%	%		%	
Rosin (Florida)	A	75	$1 + {}^1/_2$	265.4	154.9		−44.4	Nil[b]
		20	1 + 4	187.9	84.8		+18.3	
		0	1 + 7	155.0	61.8		+31.4	
	B	Lab.	18	292.7	173.3		−53.8	
		Lab.	18	285.7	163.8		−41.9	

[a] For 1 double bond and molecular weight 302. [b] According to McIlhiney.[2]

method the sample indicated its acidity quantitatively in contact with aqueous iodide–iodate, the titration due to this effect being deducted to obtain the stated substitution value zero. With cinnamic acid the total consumption of bromine in the McIlhiney method was the theoretical, and results would be excellent if the acid titration were ignored. In contact with water, iodide and iodate, however, the dibromide appeared not only to exert its effect as an acid, but also to suffer extensive hydrolytic breakdown.[24]

In the examination of abietic acid the negative and erratic results obtained by McIlhiney's method, and the rapid and persistent return of color after the acid titration seemed at first to be clear indications of interference by water, etc. The inadequacy of this explanation is shown by the fact that the aeration method at higher temperatures and in absence of water yielded negative values just as large. The improvement between 75 and 0° is relatively enormous, and the largest positive value obtained may still be a partial one, a temperature of 0° being possibly too high for normal bromination. The results indicate roughly one double bond, which duplicates the findings of certain other workers.[25] The behavior of rosin, as would be expected, is similar to that of abietic acid.

3. **Bromination of Some Other Compounds.**—Results for several other compounds of types not yet considered are given in Table IV. Examination of cumene, cymene and menthane was undertaken to study the behavior of the isopropyl group, since it seemed possible that bromination of its tertiary carbon might yield a condition susceptible to removal of bromine by hydrolysis, or to cleavage of hydrogen bromide.

TABLE IV

BROMINATION OF SOME ISOPROPYL HYDROCARBONS AND OF SOME ESTERS

Compound	Method	Temp., °C.	Time, hrs.	Atoms of bromine			% Br added	Br no. theory
				Total	Subst.	Added		
Menthane	A	75	$1 + {}^1/_2$	4.47	2.41	−0.35	−19.9	0.0
B. p. 169.0°		30	..	3.56	1.88	−0.21	−12.0	
		25	16 + 4	1.94	0.10	− .04	− 2.3	
		0	2 + 6	0.05	.02	+ .02	+ 0.1	
	B	Lab	18	.23	.08	.06	3.2	
		Lab.	18	.09	.00	.09	5.3	
Cumene	A	75	$1 + {}^1/_2$	4.37	2.18	.01	0.5	0.0
B. p. 153.3°		20	1 + 4	5.82	2.86	.08	5.1	
	B	Lab.	18	3.99	1.94	.09	5.9	
		Lab.	18	4.02	1.88	.05	3.6	
Cymene	A	75	$1 + {}^1/_2$	6.35	3.14	.06	3.6	0.0
B. p. 153.3°		0	1 + 5	4.77	2.36	.05	2.9	
	B	Lab.	18	4.77	2.74	− .73	−43.4	
		Lab.	18	3.80	2.18	− .58	−34.5	

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[24] Beilstein, 4th ed., Vol. IX, p. 518.

[25] Virtanen [*Ann.*, **424,** 163 (1921)] by a semi-quantitative method, and Shaefer [*Ind. Eng. Chem., Anal. Ed.*, **2,** 115 (1930)], by quantitative hydrogenation in the presence of palladium, both obtained results for one double bond.

TABLE IV (*Concluded*)

Compound	Method	Temp., °C.	Time hrs.	Atoms of bromine Total	Subst.	Added	% Br added	Br no. theory
Ethyl fumarate	A	75	1 + $^1/_2$	1.98	0.01	1.96	90.9	92.9
(Eastman)		20	$^1/_2$ + 5	2.03	.00	2.03	94.3	
	B	Lab.	18	1.02	.0	1.02	47.3	
		Lab.	18	1.33	.0	1.33	61.5	
Ethyl maleate	A	75	1 + $^1/_2$	1.89	.17	1.55	72.0	92.9
(Eastman)		20	$^1/_2$ + 5	0.65	.01	0.63	29.5	
	B	Lab.	18	1.80	.09	1.61	74.9	
		Lab.	18	1.45	.04	1.38	64.0	
Ethyl oleate	A	75	1 + $^1/_2$	2.78	.26	2.26	58.3	51.5
(Eastman)		25	0 + 5	2.63	.10	2.46	62.4	
	B	Lab.	18	3.19	.45	2.30	59.2	
		Lab.	18	3.02	.39	2.24	57.6	

Comments.—The addition of bromine to menthane, cumene and cymene was in all cases slight, the titrations being small (0.18 and 0.31 cc. for menthane). The negative values for cymene by McIlhiney's method were probably due to hydrolytic action. No connection between structure and behavior upon bromination is obvious in the rather unsatisfactory results obtained for these hydrocarbons.

III. The Cleavage of Hydrogen Bromide from Brominated Compounds

The bromine values obtained by the aeration procedure were for certain substances remarkably affected by temperature, the indicated addition decreasing with higher temperatures and even becoming negative in several cases. Lower temperature appeared to favor normal bromination, and was effective in producing normal values with some substances whose bromine numbers at room temperature or at 75° were useless. The total consumption of bromine (addition plus "substitution"), on the other hand, was much increased by higher temperature. Briefly stated, *at higher temperature* (*e. g.*, 75°), *when the indicated addition was at a minimum or was even negative, the total amount of bromine consumed was at a maximum.* This is illustrated by the following data taken from previous tables.

It seems unlikely that under conditions of maximum consumption of bromine an olefinic condition could escape initial saturation, but even if this were admitted it would provide no explanation for negative addition values obtained in the absence of water. A negative value can here mean only one thing: *hydrogen bromide is being produced in excess of that properly considered as hydrogen bromide of substitution.* Since the aeration procedure excluded contact of the sample with water, iodide and iodate, the production of hydrogen bromide due to hydrolysis or to other causes mentioned in the introduction can be dismissed from consideration. There remains the conclusion that hydrogen bromide may have split out

TABLE V

RELATIONSHIP BETWEEN EXTENT OF "SUBSTITUTION" AND INDICATED ADDITION VALUE

Compound	Temp., °C.	Indicated addition, % Br	Indicated "substitution," % Br
Retene	75	−11.8	255.2
	0	+67.0	129.0
Abietic acid	75	−88.1	354.0
	0	+52.5	131.6
Rosin	75	−44.4	154.9
	0	+31.4	61.8
Heavy lubricating oil	75	− 5.2	23.9
	0	+ 1.4	7.8
Transformer oil	75	− 4.3	21.6
	0	+ 0.5	4.5
Menthane	75	−19.9	274.5
	0	+ 0.1	0.2

spontaneously from a heavily brominated molecule due to instability at the existing temperature. To test this conclusion, samples of several substances were brominated at lower temperatures, freed from bromine and hydrogen bromide in the usual way, and were then heated for thirty to forty-five minutes in the aeration apparatus, any volatile products of this operation being collected in potassium iodide solution in the receiver. The solution in the receiver was treated with starch indicator (no color, showing no free bromine retained in the sample or split out on heating), iodate solution was added, and any liberated iodine was titrated. Excepting menthane, the substances so tested, exhaustively brominated at 0°, yielded hydrogen bromide when heated to 75°, and several lost hydrogen bromide on warming only to room temperature. The hydrogen bromide obtained in these experiments was not merely a qualitative trace, but in several cases approximated in amount the excess hydrogen bromide indicated by the abnormal results of analysis at the higher temperature, though no attempt was made to complete the elimination of hydrogen bromide.

The hydrogen bromide split out of two specimens of abietic acid brominated at low temperature and heated to 75°, if multiplied by two as in the analysis, and subtracted from the addition values at 0°, changes these to −59.8 and −38.6%. Similarly the "corrected" values for rosin become −24 and −1.2. The addition value for retene is in the same way reduced from 67 to 23, and that for phenanthrene from 90.8 to 60.8. It is, therefore, shown that the abnormal addition values obtained by bromination at too high temperature may be approached artificially by brominating at low temperature and then splitting out hydrogen bromide by heat.

The cleavage of HX from halogenated organic molecules is, of course, not a new idea,[26] but its possible interference with analytic brominations appears to have been overlooked. That the accumulation of negative atoms or radicals inclines molecules to instability and to cleavage is well known.[27] Cleavage of hydrogen bromide during analysis involves dehydrogenation (oxidation) of the molecule by bromine. The separation of some carbon when paraffins are chlorinated, and especially when methane and chlorine are exploded (with formation of hydrogen chloride in both cases), and many condensations by oxidation, are similar dehydrogenations. So also are such reactions as the formation of hydrogen iodide by heating rosin and iodine,[28] and of hydrogen sulfide by heating paraffin and sulfur.

The simplest result of hydrogen bromide cleavage would be the introduction of a double bond, and under conditions suitable for the saturation of double bonds. A more intimate knowledge of such reactions may show that double bonds are thus introduced in positions inaccessible to subsequent bromination, due to proximity of negative radicals, including bromine atoms firmly held,[29] or to a structural condition such as conjugation. Whatever the explanation, the fact of hydrogen bromide cleavage appears to be established, and its importance in analytic bromination is obvious.

IV. Conclusion

Tables I–IV show that in all but a few cases the aeration method, under suitable temperature conditions, yielded better results than did McIlhiney's method. It is to be noted that by proper temperature control of the brominations negative results were completely eliminated.[30]

The aeration procedure has yielded an explanation for the low or negative bromine values obtained for certain substances, since by exclusion of other sources of error it has brought into prominence the spontaneous cleavage of hydrogen bromide (other than that properly attributable to substitution) from such substances when exhaustively brominated at a

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[26] Kharasch and Darkis [*Chem. Rev.*, **5**, 601 (1928)] cite the thermal cleavage of hydrogen bromide from triphenylethylene dibromide; and the ready loss of HX from the 9,10-anthracene dihalides is familiar.

[27] See *e. g.*, Henrich (Johnson–Hahn), "Theories of Organic Chemistry," John Wiley and Sons, Inc., New York, **1922**, p. 581.

[28] Kastle and Bullock, *Am. Chem. J.*, **18**, 105 (1896).

[29] *Cf.* Cohen, "Organic Chemistry," Arnold and Co., London, **1928**, Vol. I, pp. 125–128.

[30] The accuracy of McIlhiney's method in difficult cases might be improved by operating at 0°, but some error would persist with compounds which before or after bromination are reactive with aqueous iodide–iodate. This interference, while often not important, is apparently quite general in analyses by the McIlhiney procedure, as is shown by the return of the starch–iodide color after the end-point of the acid titration. This secondary liberation of iodine was in several cases (controlled by blanks) observed to continue for weeks.

too high temperature. This conclusion was verified by experimental elimination of hydrogen bromide from several substances brominated at low temperature and then warmed to 75°.

The practical application of the findings by the aeration procedure requires the use of bromination temperatures low enough to prevent excessive consumption of bromine by reactions other than addition, and thereby to prevent or minimize spontaneous cleavage of hydrogen bromide in excess of that actually due to substitution. Some substances brominate normally at 75°, others at room temperature, while others yield entirely meaningless results unless brominated near 0°, which for some substances is perhaps still too high a temperature. The new procedure permits the necessary temperature regulation, and appears to be unique in that it permits bromination at elevated temperature and avoids complications due to contact of water, iodide and iodate with the brominated sample. There is now under investigation a new aeration apparatus designed to effect bromination with a minimal excess of bromine, thus decreasing the quantity of bromine to be transferred by aeration and shortening the analysis, especially when low temperatures are used.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY AND OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

PSEUDO BASES. I. CERTAIN N-METHYLPYRAZINIUM SALTS AND THEIR CORRESPONDING BASES

BY JOHN G. ASTON

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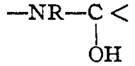
The work of Hantzsch and of Decker[1] has demonstrated that a quaternary base of the type $[-N^{+}R=C<]\ OH^{-}$ in which the $N=C$ grouping is part of a closed ring (*e. g.*, N-methylpyridinium hydroxide) may exist in two tautomeric modifications. One of these with the formula written above is a quaternary ammonium compound and therefore in aqueous solution necessarily a strong electrolyte.[2] The other weakly basic modification has the formula  $-NR-\underset{OH}{\underset{|}{C}}<$ and has been called by Hantzsch a "pseudo base;" it is a tertiary amine and has, to a certain extent, the properties of a carbinol. We shall speak of the equilibrium mixture between these two forms as a "pseudo basic system."

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[1] Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899); Decker, *J. prakt. Chem.*, **192**, 425 (1911).

[2] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, New York, **1923**, p. 111.