

residual resistance to ours, the values agree with our results to within 5% below 4000 gauss. At 8000 gauss they are about 15% lower. This would be expected since their wire had a smaller value of H_k than ours and should deviate from the square law at smaller field strengths. The observed resistance changes differ by a factor of two.

At 4.2° the gold wire investigated by Meissner and Scheffers showed a decrease in resistance for fields less than 200 gauss and an increase for larger fields. This effect was ascribed to ferromagnetic impurities. Because of this effect and since the measurements of Meissner and Scheffers extended only to 600 gauss, it is difficult to make comparison with our results.

The single crystals of gold investigated by Meissner and Scheffers had much lower values of H_k . It also has been found recently by Justi and Scheffers¹¹ that the magnetic change in resistance of single crystal gold is strongly influenced by the orientation of the magnetic field with respect to the crystal axes. For these reasons no

(11) Justi and Scheffers, *Physik. Z.*, **37**, 383, 475 (1936).

comparison with our results has been attempted.

We thank Prof. W. F. Giauque for his advice and assistance with the measurements.

Summary

The electrical resistances of gold and silver wires have been measured at temperatures ranging from 1.5 to 20°K. and in magnetic fields from zero to 8000 gauss. For the silver wire at the lowest temperatures both the resistance and its magnetic coefficient are independent of temperature. As the temperature rises the resistance increases and the magnetic coefficient of resistance decreases. The gold wire has a minimum in resistance at about 7.7°K. The magnetic coefficient of resistance is a maximum at this temperature. The magnetic field tends to eliminate the minimum in resistance. Extrapolation of the measurements indicates that at 1°K. the magnetic coefficient would become zero and below this temperature would be negative. Such a negative coefficient of resistance has been found previously in another sample of gold wire.

BERKELEY, CALIF.

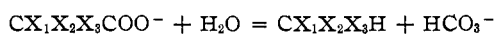
RECEIVED NOVEMBER 2, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Rate of the Haloform Reaction. Effect of the Nature of the Halogens

BY L. H. SUTHERLAND AND J. G. ASTON

The rate of the reaction



where $X_1 = X_2 = X_3 = Br$, has been studied by DeGroot¹ at 25°, and by Fairclough² at several temperatures and, where $X_1 = X_2 = X_3 = Cl$, by Verhoek.³ All found that this reaction was unimolecular with respect to the ion. The tribromo compound was studied only in water by both investigators. The trichloro was studied at several temperatures in several solvents.³ The rate depended on the solvent but in all cases the reaction was essentially of the first order.

At 25° in water the tribromoacetate ion undergoes by far the more rapid cleavage, the cleavage of the trichloro being hardly detectable at that temperature. The energy of activation of the former was 24,100, and of the latter 36,600³ cal. per mole.

(1) DeGroot, *Bull. soc. chim. Belg.*, **37**, 225 (1928).

(2) Fairclough, *J. Chem. Soc.*, 1186 (1938).

(3) Verhoek, *THIS JOURNAL*, **56**, 571 (1934).

For both practical and theoretical reasons data on the cleavage of trihaloacetic acids are desirable. In the present paper data are presented on chlorodibromoacetic acid and some preliminary data on chlorobromofluoroacetic acid. The rate of cleavage of the first of these is of the first order and depends only on the concentration of the chlorodibromoacetate ion. The average specific reaction rate constants (Col. 6) for runs with

TABLE I
HALOFORM REACTION OF SODIUM CHLORODIBROMOACETATE
AT 60°

T , °C.	Starting concn. of haloacetate moles/liter	Excess NaOH moles/liter	Fraction reacted at end	Ratio hydrolysis to haloform reaction	Av. $k_1 \times 10^5$, sec. ⁻¹
60.2	0.1210	0.0121	45	1:15	7.2
60.2	.0630	None	45	1:50	8.6
60.7	.0288	None	60	1:50	7.7
60.7	.0875	0.0088	60	1:25	7.7
60.7	.0566	.0057	60	1:25	8.6

Av. 8.0

several starting concentrations (Col. 2) and varying excesses of alkali (Col. 3) in water at 60° are summarized in Table I.

The percentage of the compound from which halogen was hydrolyzed, as estimated by Volhard halogen determination (Col. 5), did not exceed 6% of the quantity reacted as determined by carbonate analysis. A blank experiment on the haloform itself indicated that most, if not all, of the halide came from this source. Therefore no correction to the concentration of unreacted compound was made. The inaccuracy of determination of the small amount of halide formed prevented any conclusions being drawn from the rate of its production.

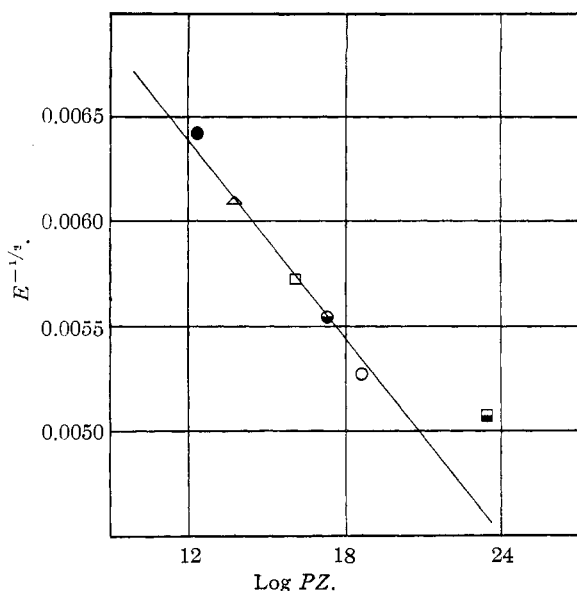


Fig. 1.—Dependence of PZ on E for the decarboxylation of certain trihaloacetate ions in various solvents.

	Water	Ethanol	Aniline (Solvent)
Cl_3CCOO^-	○	□	△
$\text{ClBr}_2\text{CCOO}^-$	●	■	
Br_3CCOO^-	●		

The data at other temperatures are similar. In Table II are given the average constants at the various temperatures investigated. The energies of activation in the last column were calculated from the integrated Arrhenius equation over the intervals given in parentheses. These results are consistent with an essentially constant energy of activation of 32,600 cal. The data in alcohol at 32 and 44° are presented in Table III, which corresponds to Table I.

The cleavage of the chlorobromofluoroacetate ion is much slower at equivalent temperatures,

TABLE II
DECOMPOSITION RATE OF THE CHLORODIBROMOACETATE ION IN WATER

Temp., °C.	k_1 , sec. ⁻¹	E , cal.
77	8.6×10^{-4}	
60	8.0×10^{-5}	32,400 (60-77)
45	7.3×10^{-6}	33,400 (45-60)

$\log_{10} k = 17.3 - (32,600/2.3RT)$

TABLE III
RATE OF DECOMPOSITION OF THE CHLORODIBROMOACETATE ION IN ALCOHOL

T , °C.	Starting concn. of halo-acetate moles/liter	Excess NaOH	Fraction reacted at end	Ratio of hydrolysis to haloform reaction	Av. k_1 , sec. ⁻¹
31.8	0.0304	None	80	...	2.5×10^{-5}
44.5	.0328	None	70	1:0	3.3×10^{-4}

$E = 39,000 \text{ cal.}; \log_{10} k = 23.4 - (39,000/2.3RT)$

and the fact that the halogens are hydrolyzed from either the ion or the haloform produced renders the data difficult to interpret. For convenience, these data are given in the experimental section in Table VI. The haloform reaction appears to be sensitive to hydroxide ion catalysis. In Tables II and III are given the equations of the form

$$\log k = \log PZ - E/2.3RT \quad (1)$$

which best fit the experimental data. Fig. 1 shows $\log PZ$ plotted against $E^{-1/2}$ using our own data and data from sources already mentioned. This graph is excellent confirmation of the ideas of Fairclough and Hinshelwood.⁴ It is to be noticed that points for the solvents water, alcohol and aniline lie on the same curve, which indicates that the effect of the solvent on PZ and E is of quite a similar nature to that of the polarity of the halogens themselves and perhaps that the cleavage reaction is facilitated by coördination with solvent in much the same way as it is by the polarity of the substituted halogens.

The fact that three chlorine atoms introduced into the acetate ion very greatly facilitate a cleavage points to an inductive effect, in which the electrons of the C-C bond are displaced toward the halogens, as the factor aiding cleavage. This, however, cannot be the sole cause, as replacement of the chlorine atoms by bromine further increases the rate in spite of the decreased negativity of the bromine, which would be expected to act in the opposite direction. The bromine atom is bigger and it must be that the reduction

(4) Fairclough and Hinshelwood, *J. Chem. Soc.*, 538 (1937).

TABLE IV
 COMPARATIVE RATES OF CLEAVAGE OF TRIHALOACETATE IONS k_1 (sec.⁻¹)

Temp., °C.	CIBrF	Cl ₃	CIBr ₂	Br ₃
25		4.6×10^{-9} ^a (extrap.)	2.5×10^{-7} (extrap.)	5.7×10^{-7} ^b 3.3×10^{-8} (extrap.) ^c
60		3.5×10^{-6} ^a	8×10^{-5}	2.3×10^{-4} ^c
70	1×10^{-6}	1.7×10^{-5} ^a	3×10^{-4}	5.4×10^{-4} ^c

^a Data by Verhoek.³ ^b Data by DeGrootte.¹ ^c Data by Fairclough.²

in negativity is offset by the part played by the unshared electrons. The $\log PZ$ vs. $E^{-1/2}$ plot may indicate that the part thus played by these electrons is similar to that of those of the solvent molecules in modifying the rate.

Table IV summarizes for completeness the first order rate constants for tribromo-, chlorodibromo-, trichloro-, and chlorobromofluoroacetate ions—either observed or calculated by substitution of the activation energy, E , from equation 1.

Experimental

Preparation and Purification of Compounds.—

The chlorodibromoacetic acid used in most experiments was prepared and purified by the method of Swarts,⁵ m. p. 89.5–90.5° (Swarts gives 89°). In the experiments at 32° in alcohol, a sample recrystallized from petroleum ether (b. p. 60–90°) was used. The melting point of this sample was 100.5°.

The chlorobromofluoroacetic acid was also prepared and purified by the method of Swarts.⁵ The material used boiled at 85.5° at 22 mm.; mol. wt., calcd. for C₂HO₂BrClF, 191; found, (neut. equiv.) 198, (Stepanow-Volhard) 191.

The reaction was run in sealed tubes in an oil thermostat held at the respective temperatures to $\pm 0.1^\circ$ below 65° and to $\pm 0.2^\circ$ above 65°. The reaction was stopped at will by chilling the tubes in ice and salt. The extent of the haloform reaction was determined by the difference between the end-points of phenolphthalein and brom phenol blue. Experiments run in both the presence and absence of air proved that oxygen is without effect, so that no effort was made to exclude air in the later experiments. The halide formed was determined by Volhard titration. In Table V is given a portion of the data from one run on the chlorodibromoacetate ion, and in Table VI are given samples of the data from two runs on the chlorobromofluoroacetate ion.

(5) Swarts, "Mémoires Couronnés et Autres Mémoires par l'Académie Royal des Sciences, des Lettres et des Beaux-Arts de Belgique," t54 (1896).

TABLE V

SAMPLE	RUN ON	THE CHLORODIBROMOACETATE ION				
		Time, min. $t/60$	Concn. (C) $\text{ClBr}_2\text{C}_2\text{O}_2^-$	Concn. total halide ion $\times 10$	Log ₁₀ C/C ₀ ^a $+1.000$	Deviation of log ₁₀ C/C ₀ from the line log ₁₀ C/C ₀ = $-8.6 \times 10^{-3}t$
		0	0.0566	0.010	1.000	...
		10	.0548	.011	0.986	0.008
		30	.0490	.014	.937	.004
		45	.0452	.017	.902	.003
		80	.0375	.027	.820	-.001
		130	.0292	.040	.712	+.004
		195	.0222	.048	.592	+.030

^a C = C₀ when t = 0 in all runs.

TABLE VI

Time, min. $t/60$	Concn. ^a (C) $\text{ClBrFC}_2\text{O}_2^-$	Total halide ion concn.	Log ₁₀ C/C ₀ ^b $+1.000$	Deviation of log ₁₀ C/C ₀ from log ₁₀ C/C ₀ = $-8.7 \times 10^{-3}t$
				from log ₁₀ C/C ₀ = $-2.6 \times 10^{-3}t$
(a) 0	0.0440	...	1.000	...
150	.0432	0.0023	0.992	-0.005
720	.0425	.0063	.985	+.001
1140	.0415	.0069	.974	.000
1350	.0408	.0078	.967	-.002
1575	.0405	.0105	.964	.000
(b) 0	0.0400	0.0005	1.000	...
246	.0385	.0030	0.983	0.000
516	.0371	.0048	.967	.002
1221	.0315	.0112	.896	-.021
1221	.0331	.0097	.918	.001

^a This calculated only from the concn. of carbonate ion formed. ^b See note to previous table.

To obtain the average value of k_1 for any run the logarithm of the concentration was plotted against the time. The slope of the best straight line through the points yielded the average value directly.

Summary

1. The rate of the haloform reaction for chlorodibromoacetate ion has been measured at several temperatures in water and alcohol and found to be of the first order, but not independent of the solvent. The energy of activation has

been calculated to be 32,000 cal. in water and 39,000 cal. in alcohol.

2. The rate of the reaction of chlorobromo-fluoroacetate ion has been measured but not interpreted. It is influenced by hydroxide ion.

3. The dependence of the *PZ* factor on the

energy of activation has been discussed for this type of reaction.

4. The effect of the nature of the halogens and of the solvent on the rate has been discussed.

STATE COLLEGE, PENNA.

RECEIVED OCTOBER 31, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of 6-Chloro-10-methyl-1,2-benzanthracene and Related Compounds

BY MELVIN S. NEWMAN AND MILTON ORCHIN

As part of a coöperative study¹ on the effect of certain functional groups on the carcinogenic activity of 10-methyl-1,2-benzanthracene this Laboratory has previously reported the synthesis of 7-² and 5-chloro-10-methyl-1,2-benzanthracene³ and some related compounds. The results of biological experiments⁴ show that the presence of a chlorine atom in the 5- or 7-position or a cyano group in the 7-position causes considerable diminution of the carcinogenic activity of the parent compound. The amide of 5-carboxy-10-methyl-1,2-benzanthracene as well as 7-carboxy- and 7-carbomethoxy-10-methyl-1,2-benzanthracene are inactive. However, 5-cyano-10-methyl-1,2-benzanthracene rates with the parent hydrocarbon as one of the most potent sarcoma producing compounds known.⁵ In view of the interesting results obtained with these variously substituted 10-methyl-1,2-benzanthracenes, we have prepared and now report the synthesis of 6-chloro-10-methyl-1,2-benzanthracene and its conversion to 6-cyano, 6-carboxy, and 6-carbomethoxy-10-methyl-1,2-benzanthracene.

The method of synthesis was entirely analogous to that employed in the preparation of the isomeric 7- and 5-substituted compounds.^{2,3} The final step in the present work consisted in the cyclization of 2-(α -methyl-*m*-chlorobenzyl)-1-naphthoic acid, I, to the corresponding unstable anthrone and the reduction of this to 6-chloro-10-methyl-1,2-benzanthracene, II.

It was possible, but deemed unlikely, that ring closure of the acid, I, took place in the position

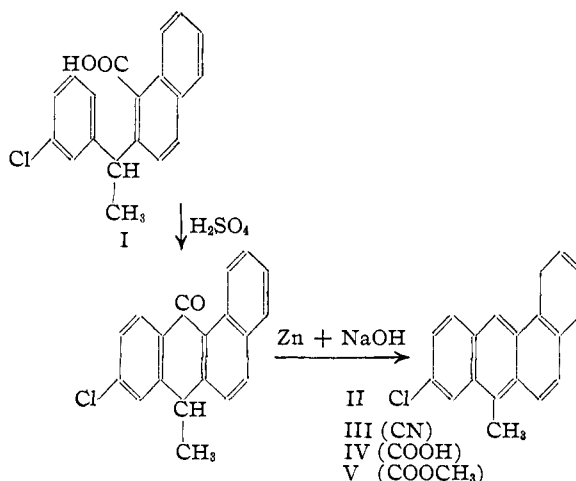
(1) All the animal experimentations were performed by Dr. M. J. Shear, whose latest summary of the results obtained appears in *Am. J. Cancer*, **33**, 499 (1938).

(2) Newman and Orchin, *THIS JOURNAL*, **60**, 586 (1938).

(3) Newman, *ibid.*, **60**, 1368 (1938).

(4) Private communication from Dr. M. J. Shear.

(5) For a complete summary of the chemistry of the cancer producing compounds see Fieser, *Am. J. Cancer*, **34**, 37 (1938).



ortho to the chlorine atom, in which case the final compound would be the isomeric 8-chloro-10-methyl-1,2-benzanthracene. In order to establish the structure of the final compound, II, it was oxidized to a chloro-1,2-benzanthraquinone and this quinone shown to be identical with an authentic sample of 6-chloro-1,2-benzanthraquinone prepared from the known¹ 1-*p*-chlorobenzoyl-2-naphthoic acid, VI. The anthrone resulting from the ring closure of the crude product obtained on sodium amalgam reduction of VI was immediately reduced to 6-chloro-1,2-benzanthracene, VII. Oxidation of VII produced in good yield a quinone identical with that obtained from the oxidation of the compound produced through cyclization of 2-(α -methyl-*m*-chlorobenzyl)-1-naphthoic acid, I. This indicates that the compound resulting from the cyclization of I is indeed substituted in the 6-position.

All attempts⁶ to cyclize the keto acid directly to the quinone, VIII, were unsuccessful. In one experiment, using a melt of aluminum chloride-

(6) Waldmann, *J. prakt. Chem.*, **150**, 121 (1938).