REACTIVITY OF HALOGENS IN ORGANIC COMPOUNDS. PART VI. 1049

CX.—Reactivity of the Halogens in Organic Compounds. Part VI. The Mechanism of Negative Catalysis.

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In the latest paper of this series (this vol., p. 45) the results of an experimental investigation of the rate of reaction between silver nitrate and the esters of bromo-substituted fatty acids were communicated. The kinetics of the reactions of silver nitrate with bromoacetic and bromopropionic acids respectively have now been investigated, and the results are given in the present paper. The nitric acid formed in the course of the reaction retards the change to an even greater extent than in aqueous solution (compare Trans., 1910, 97, 346). This is to be regarded as an example of negative catalysis, and in the course of the investigation it has been found that the generally accepted method of representing negative catalysis (Ostwald, Allgemeine Chemie, II, 2, 270) is not in accord with the available experimental data. On the basis of the experimental results communicated in the present paper, and also of the data already obtained for the retardation of the hydrolytic decomposition of the bromo-fatty acids by the hydrobromic acid formed in the course of the reaction (Senter, Trans., 1909, 95, 1827), suggestions for the mathematical representation of negatively catalysed reactions are put forward.

Experimental.

The measurements were carried out as described in the previous paper dealing with the esters (*loc. cit.*). The solutions were warmed separately in the thermostat, and then mixed in a number of small tubes. At definite intervals, the contents of a tube were transferred to a beaker containing a slight excess of N/50-ammonium thiocyanate, and the excess of thiocyanate then estimated by means of N/50-silver nitrate.

If there were no retarding effect due to the nitric acid, the reactions would be approximately bimolecular. In order to illustrate the magnitude of the retardation, the velocity-coefficients are calculated by the ordinary formula for a bimolecular reaction, and are represented in the tables by k_{bimol} . As in previous papers, the coefficients are referred to a concentration of $1/(12 \times 50)$ mols. per litre, and in order to refer them to a concentration of 1 mol. per litre must be multiplied by 600. The unit of time is one minute

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throughout. The majority of the experiments were made at 49.9° ; a few at 26° .

TABLE I.

Temperature 49.9°.

Solvent: Ethyl alcohol.			Solvent: Methyl alcohol.			
Bromoacetic acid, N/20.			Bromoacetic acid, $N/20$.			
Silver nitrate, $N/20 \times 0.98$.			Silver nitrate, $N/20 \times 1.05$.			
t (min.).	t (min.). $a-x$. kbimol. $\times 10^4$.			a - x. kbimol. × 1		
0	29.5		0	31.4		
15	28.45	0.83	15	30.5	0.84	
45	27 2	0.63	45	28.7	0.62	
135	24.4	0.2	135	26.25	0.46	
405	19.45	0.43	405	21.95	0.34	
Bromopr	opionic acid	d , <i>N</i> /20.	Bromopre	opionic ae	id, N/20.	
Silver n	itrate, $N/2$	0×0 99.	Silver ni	trate, $N/$	10×1 04.	
t (min.).	a - x. k	bimol. $ imes 10^4$.	t (min.).	a - x.	$k imes 10^4$.	
0	29.5		0	31.1		
5	24.9	12.5	5	27.6	9.5	
15	20.85	9.4	15	25.2	5.1	
45	17.7	5.0	45	22.3	2.8	
135	14.0	2.8	135	18.3	1.7	

Temperature 26°. Solvent: Ethyl Alcohol.

Bromopropionic acid,	$egin{array}{c} N/20 \ N/20 \end{array} \}$	a - x from 30.0 to 24.0 c.c. in	k×10 ⁴ from
Silver nitrate		180 minutes.	1.52 to 0.46.
Bromoacetic acid, Silver nitrate,	$\left. \begin{smallmatrix} N/10 \ N/20 \end{smallmatrix} ight\}$	$\alpha - x$ from 30.0 to 18.0 c.c. in 2400 minutes.	$\begin{cases} k \times 10^4 \text{ from} \\ 0.051 \text{ to } 0.041. \end{cases}$

Solvent: Methyl Alcohol.

Bromopropionic acid, N/30 a-x from 20.0 to 18.45 c.c. $k \times 10^4$ from Silver nitrate, N/30 in 90 minutes. f 1.3 to 0.5.

Apart from the gradual fall in the magnitude of the velocity coefficients, the above results illustrate two important facts. In the first place, the rate of reaction between a bromopropionic acid and silver nitrate is rather less in methyl and in ethyl alcohol, both at 49.9° and at 26° . In an earlier paper (*loc. cit.*, p. 352) it was shown that the velocity of the same reaction is practically the same in water and in 50 per cent. alcohol, so that it is nearly independent of the nature of the solvent. The esters, on the other hand, react with silver nitrate more rapidly in methyl than in ethyl alcohol (*loc. cit.*, p. 100).

The second point has reference to the magnitude of the temperature-coefficients of the reaction velocity. Calculating from the same stages of the respective reactions, it is seen that the rates of both reactions are increased about nine times by raising the temperature from 26.0° to 49.9° , so that the average coefficient for 10° is about 2.5. This is exactly the same as for the esters (*loc. cit.*, p. 100).

Before entering on a discussion of the mechanism of the reactions, it is important to find whether any error arises from esterification of the acids while measurements are being made. This would, of course, modify the reaction velocity, as the esters are throughout less active than the corresponding acids. The results of some experiments in ethyl alcohol at 49.9°, in which nitric acid was used as catalytic agent, are given in the accompanying table.

TABLE II.

Bromopropionic acid, Nitric acid,	$\left. \begin{smallmatrix} N/10 \ N/20 \end{smallmatrix} ight\}$	$k \times 10^4 = 0.033.$
Bromoacetic acid, Nitric acid,	$\left. egin{smallmatrix} N/10 \ N/20 \end{smallmatrix} ight\}$	$k \times 10^4 = 0.072.$

The velocity constants quoted represent the rate of esterification during the first two or three hours—the duration of the experiments. In the later stages of esterification the constants become considerably greater. The data show that esterification does not become appreciable in the comparatively fast reaction between silver nitrate and bromopropionic acid, but may exert some influence on the much slower reaction between silver nitrate and bromoacetic acid. In applying these results to elucidate the nature of negative catalysis, only the measurements with bromopropionic acid are taken into account.

Since the falling off in the magnitude of the velocity constants as the reaction proceeds has been ascribed to the accumulation of nitric acid in the system, it is of interest to find the effect of adding nitric acid at the beginning of the reaction. A solution of the acid in absolute alcohol was therefore prepared by adding to a solution of silver nitrate in alcohol just sufficient of an alcoholic solution of hydrogen chloride to precipitate all the silver. The results of the experiments are given in the accompanying table.

TABLE III.

Bromopropionic acid, <i>N</i> /20. Nitric acid, <i>N</i> /40.			Silver nitrate, <i>N</i> /20. Nitric acid, <i>N</i> /80.			
0	29.5		0	29.5	_	
20	27.85	1.00	10	28.15	1.9	
60	25.4	0.92	30	25.2	1.9	
120	22.9	0.85	60	23.2	1.5	
240	19.2	0.75	120	20.3	1.3	

The data show that the retardation due to the nitric acid is, in the first instance, proportional to the amount of the acid added. VOL. XCIX. 3 Y

The magnitude of the retardation is very striking; N/40-nitric acid reduces the speed to about one-fifteenth of its original value. The effect is much greater than for the corresponding reaction in aqueous solution (loc. cit., p. 351), in which circumstances N/15-nitric acid reduces the speed to about one-seventh of the original. This is in entire accord with the view as to the mechanism of the reaction advocated in the previous paper, as the difference in the strengths of nitric and of bromopropionic acid is much greater in alcoholic than in aqueous solution (compare Godlewski, Bull. Acad. Sci. Cracow, 1904, 6, 239; Baly, Burke, and Marsden, Trans., 1909, **95**, 1096).

The next point to be taken into consideration is whether the amount of acid formed is equivalent to that of the silver nitrate used up. The matter was investigated by simultaneous titration of the silver nitrate remaining and of the nitric acid formed as the reaction proceeded. For the latter purpose, the reaction mixture was added to an excess of potassium bromide solution to remove the silver nitrate, and the mixture then titrated with N/20-sodium hydroxide solution in the usual way. The results of one series of measurements, referred to the same standard of concentration, are given in the accompanying table.

TABLE IV.

<i>t</i> (min.).	AgNO ₃ used no.	HNO ₃ formed.	Ratio HNO ₂ /AgNO ₂ .
0	0.0	0.0	
5	4.6	3.0	65 per cent.
15	8.05	5.4	67
45	11.8	7.5	63 .,
135	15.5	9.3	61

The figures show that the amount of nitric acid set free is about two-thirds of that of the silver nitrate used up, and that the ratio remains practically constant throughout the change. The simplest interpretation of these observations is that the silver nitrate is being used up in two simultaneous reactions, in one of which no nitric acid is liberated.

When bromopropionic acid and silver nitrate are mixed, we may assume with certainty that the following equilibrium is immediately established:

 $CHMeBr \cdot CO_2H + AgNO_3 \rightleftharpoons CHMeBr \cdot CO_2Ag + HNO_3$. . (1)

In the light of the above results, the two simultaneous reactions: $CHMeBr \cdot CO_2Ag + C_2H_5 \cdot OH \longrightarrow CHMe(O \cdot C_2H_5) \cdot CO_2H + AgBr (2)$ $CHMeBr \cdot CO_2H + AgNO_8 + 2C_2H_5 \cdot OH \rightarrow$

 $CHMe(O \cdot C_2H_5) \cdot CO_2H + AgBr + C_2H_5 \cdot NO_3 (3)$

may then be assumed to occur. In reaction (2) an amount of

nitric acid is liberated equivalent to that of the silver nitrate used up; in reaction (3) no nitric acid is formed. The method of representing the results mathematically is dealt with in the next section on negative catalysis.

Negative Catalysis.

The results communicated in the present paper, and those obtained for the decomposition of the bromo-fatty acids by water, for example, bromopropionic acid, as represented by the equation:

 $CH_{a} \cdot CHBr \cdot CO_{2}H + H_{2}O \longrightarrow CH_{a} \cdot CH(OH) \cdot CO_{2}H + HBr$

throw considerable light on the question of negative catalysis, especially of negative autocatalysis, a branch of chemical dynamics which has hitherto been very much neglected. The mathematical representation of negative catalysis generally accepted is that given by Ostwald (*loc. cit.*, p. 270). For a unimolecular reaction, the differential equation takes the following form:

$$\frac{dx}{dt} = k_1(a-x) - k_2 x(a-x),$$

where the symbols have the usual significance. In the simplest case here dealt with, a would represent the initial concentration of the bromopropionic acid, and x that of the negative catalyst, the hydrobromic acid, formed in the course of the reaction.

It is evident from the form of the above equation that when the ratio k_2/k_1 is sufficiently large, dx/dt becomes zero; in these circumstances, the reaction will come to an end before decomposition is complete, and, further, it will not approach the end-point in an asymptotic manner, as in the great majority of reactions which have been carefully investigated. Now there does not appear to be any experimental evidence of the occurrence of a "false equilibrium" of this nature in a homogeneous system, and it will be evident from what follows that Ostwald's formula is incompatible with the experimental results obtained for negatively catalysed reactions in this and the previous papers of the series.

The method of formulating the hydrolytic decomposition of bromopropionic acid will now be considered on the assumption (compare Senter, Trans., 1909, **95**, 1836) that both the CHMeBr· CO_2' ions and the non-ionised acid undergo change. The equations are as follows:

$$CHMeBr \cdot CO_{2}H \Longrightarrow CHMeBr \cdot CO_{2}' + H'$$

$$a - x \qquad \eta \qquad \xi$$

$$CHMeBr \cdot CO_{2}H + H_{2}O \longrightarrow CHMe(OH) \cdot CO_{2}H + H' + Br'$$

$$[H'] + CHMeBr \cdot CO_{2}' + H_{2}O \longrightarrow [H'] + CHMe(OH) \cdot CO_{2}H + H'.$$

$$y_{2}$$

$$3 \times 2$$

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The concentrations of the various substances present at the time t, expressed in the usual way, are given below the respective formulæ. The initial concentration of the acid, as determined by titration (thus including both ionised and non-ionised acid), is represented by a. What is measured in this case is the rate at which the total acidity of the solution increases; the difference between total acidity at any time and initial acidity, which is a measure of the total rate of hydrolytic decomposition, is expressed on the above basis by y_1+y_2 . It is, of course, assumed that the establishment of the equilibrium between the acid and its ions is instantaneous.

The equations connecting the different variables are as follows:

$$\frac{\eta\xi}{a-x} = c; \quad \frac{dy_1}{dt} = k_1(a-x); \quad \frac{dy_2}{dt} = k_2\eta$$
$$x = \xi = \eta + y_1 + y_2,$$

as will be evident without further explanation. The integral of these equations has the following form:

$$-\left[\frac{k_2^2c}{k_1^2}+a\right]\log_e\left(x+\frac{k_2c}{k_1}\right)-\frac{(a+c)k_2}{k_1}\log_e(a+x)+\\\left(a+\frac{k_2c}{k_1}\right)\log_e x=k_2\left(a+\frac{k_2c}{k_1}\right)t+\text{constant.}$$

Of the factors of this equation, c, which is proportional to the dissociation constant of bromopropionic acid (assumed to be 0.00108 at 79°), is 0.131; k_1 , the rate of hydrolysis of the non-ionised acid, has already been obtained by measurements in the presence of excess of hydrobromic acid: it amounts to 0.00053 at 79°; a is 11.8; and the only unknown is k_2 , the velocity coefficient for the reaction between CHMeBr·CO₉' ions and water.

The most severe test of the applicability of the equation is to use it for the case in which no hydrobromic acid is added at the commencement of the reaction (table V, columns 1 and 2). The last column contains the values of the velocity coefficient calculated for a reaction of the first order—as is to be anticipated, they diminish rapidly during the reaction.

TABLE V.

t.	$C_t = a - (y_1 + y_2).$	$y_1 + y_2$ (obs.).	$y_1 + y_2$ (calc.).	x.	kunimol.
0	11.8	0.0	0.0	1.18	
120	8.8	8.0	2.85	$3 \cdot 2$	0.0024
240	7.3	4.5	4.4	4.6	0.0019
360	6.3	5.2	5.45	5.6	0.0012
1380	2.2	9.6	9.2	9.2	0.0010

It has now been found that the equation is almost exactly satisfied by putting $k_2 = 0.030$. One test is that when the left

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hand side of the equation is plotted against t, a straight line is obtained, as the equation requires, and, further, the slope of the line agrees with the value $\bar{k}_2(a+ck_2/k_1)$. Another test is to find by successive approximations the values of x which satisfy it for different values of t, and from these calculating the values of $y_1 + y_2$ by means of the equations $\eta x/(a-x) = c$ and $y_1 + y_2 = x - \eta$ connecting the variables. The observed and calculated values of $y_1 + y_2$ are given in the third and fourth columns of the table, and it will be seen that the agreement is excellent. The velocity coefficient, k_2 , of the hydrolysis of the CH₃·CHBr·CO₂' ion can also be obtained entirely independently from the rate of hydrolysis of sodium bromopropionate by water. The value thus obtained is 0.035 (loc. cit., p. 1836), which, considering the slight uncertainty as regards the temperature-coefficient of hydrolysis, is in very good agreement with the above value, 0.030. The simple assumptions made in deducing the above formula are therefore justified, and the alternative suggestion of Bodenstein (Zeitsch. Elektrochem., 1909, 15, 403) as to the mechanism of these reactions does not apply.

We now come to the reaction between silver nitrate and bromopropionic acid in alcoholic solution. The first stage in this case is undoubtedly the instantaneous establishment of the equilibrium :

$CHMeBr \cdot CO_2H + AgNO_3 \rightleftharpoons CHMeBr \cdot CO_2Ag + HNO_3$.

As regards the further progress of the reaction, different assumptions might be made. Without going into the matter fully, we may assume, on the basis of the simpler reaction just considered, that the velocity is proportional to the concentrations of the silver nitrate and acid respectively, and inversely proportional to the nitric acid concentration at the time t. Further, since in alcoholic solution nitric acid is a very much stronger acid than *a*-bromopropionic acid (p. 1052), there will be no appreciable error in taking its concentration at any time, t, as that liberated in the reaction $(\frac{2}{3}x, \text{ compare p. 1052})$. The differential equation on this basis is therefore:

$$d\boldsymbol{x}/d\boldsymbol{t} = \boldsymbol{k}(\boldsymbol{a} - \boldsymbol{x})^2/\frac{2}{3}\boldsymbol{x},$$

which, on integration, and taking x=0 when t=0, becomes:

$$\frac{x}{a-x} - \log_e \frac{a}{a-x} = \frac{3kt}{2}$$

The results of the calculation of the experimental data according to this equation are given in table VI.

TABLE VI.

t	0	5	15	45	135
a - x	29.5	24.9	21.45	17.7	14.0
k	—	0.0021	0.0024	0.0023	0.0017

The coefficients for the greater part of the reaction are nearly constant, and proved the applicability of the formula. The fall after one hundred and thirty-five minutes is probably due to some secondary reaction, for example, to esterification of the bromopropionic acid. The equation was further tested by applying it to the case where nitric acid was added at the beginning of the reaction. The coefficient in this case was 0.0021, in good agreement with the above results.

General Considerations.—The reaction between bromopropionic acid and water is complicated by the fact that both the ions and the non-ionised acid undergo decomposition. A simpler case would be that in which only the ion undergoes hydrolysis. Representing the general formula of a monobasic acid by HA, we have the following equations:

HA
$$\rightleftharpoons$$
 H[•] H[•] H[•]
 $a - x \qquad \xi \qquad \eta$
A' + H₂O $\rightarrow Z$ + H[•].
 $\eta \qquad y$
As before, $\eta \xi / (a - x) = c$ and $x = \xi = y + \eta$,
therefore:
 $\frac{dy}{dt} = k\eta = kc(a - x)/\xi$,

that is, the rate of the reaction (the rate at which y is formed) is inversely proportional to ξ , the concentration of the negative catalyst.

If the acid is only slightly ionised, we can put dx/dt = dy/dt without serious error, and the equation can then readily be integrated. If, on the other hand, the degree of dissociation is not small, it will in general be possible to integrate the equation on the basis of some relationship between the different factors found experimentally.

It appears justifiable to extend these considerations to the phenomenon of negative catalysis in general. It has been shown that the representation of this type of catalysis as a difference between two factors (p. 1053) is not generally applicable. An empirical equation which in certain cases at least is in accordance with the experimental facts, may be based on the assumption that the rate of reaction is proportional to the respective concentrations of the reacting substances, and inversely proportional to the concentration of the negative catalyst. The only satisfactory case met with, apart from the foregoing, in which a formula of this type has been

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used, is the hydrolytic decomposition of bromosuccinic acid by water, investigated by Müller (*Zeitsch. physikal. Chem.*, 1902, **41**, 483), but the author has not drawn from his observations any general conclusions regarding negative catalysis.

In the ideal type of positive catalysis, it is assumed that the catalyst does not alter the free energy of the reacting substances. In many cases of positive catalysis, however, the free energy is undoubtedly altered, although perhaps only to a slight extent. In the examples of negative catalysis quoted in the present paper, and perhaps in all cases of negative catalysis, the free energy of the reacting substances is diminished by the presence of the catalyst. According to the view here advocated, a negative catalyst acts by diminishing the active mass of one or more of the reacting substances. The method used in obtaining accurate mathematical formulæ on this basis will be evident from the first example quoted in the present paper (p. 1053).

Catalytic Action of Colloidal Silver Bromide.

In a previous paper it has been shown that freshly formed silver bromide has a powerful catalytic effect on the reactions between silver salts and organic halogen compounds in aqueous solution, and it was suggested that the effect might be due to the silver bromide in colloidal solution. Direct evidence has now been obtained on this point by using gelatin as a protective colloid in this way the coagulation of the silver bromide is entirely prevented. In the following table are given the results of two parallel experiments, the only difference being that one solution contained 0.25 per cent of gelatin.

TABLE VII.

Bromoacetic acid, $N/20$. The Gelatin, 0.25 per cent.			Silver nitrate, N/20. No gelatin.		
t (min.).	$\alpha - x$.	k.	t (min.).	a-x.	k.
0	30.0		0	30.0	
30	27.9	0.0025	30	28.7	0.0015
60	25.45	0.0032	60	27.6	0.0013
120	20.55	0.0040	120	$25 \cdot 2$	0.0016
240	14.1	0.0038	240	21.25	0.0015
360	10.9	0.0024	360	18.75	0.0011

The results show very clearly the increase in the velocity coefficients when gelatin is present. The effect appears to depend on the gelatin concentration, as the reaction was considerably slower when only one-third of the above proportion was used. In this case, however, the silver bromide coagulated to some extent

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towards the end of the reaction. The matter is being further investigated.

Summary of Results.

The kinetics of the reactions of silver nitrate with bromoacetic and α -bromopropionic acids respectively in absolute alcohol have been measured at 49.9°. The reactions are retarded by nitric acid to an even greater extent than in aqueous solution. A formula which represents the results fairly satisfactorily is given.

A formula which represents accurately the decomposition of bromopropionic acid by water has been derived on the assumption that both the anions and the non-ionised acid react with water.

It is shown that the usual formula which represents negative catalysis as a difference between two factors is not in accordance with the available experimental data. An empirical formula, based on the assumption that the rate of reaction is inversely proportional to the concentration of the negative catalyst, is shown to represent the experimental results very closely. The mode in which accurate formulæ representing negative catalysis may be derived is indicated, and the connexion between the accurate and empirical formulæ pointed out.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed most of the expense of this investigation.

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