[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A QUANTITATIVE STUDY OF THE SO-CALLED "POSITIVE HALOGEN" IN KETONES AND ESTERS

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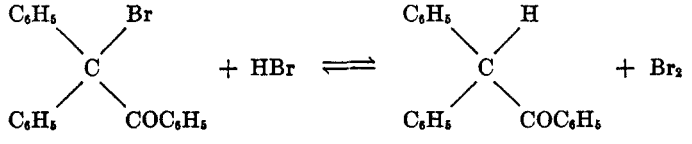
Many cases are known in which halogen, especially when in the alpha-position to one or more carbonyl groups, undergoes replacement by hydrogen in the presence of ammonia (1), amines (2), hydrazine (3), alcoholic alkalies (4), organometallic compounds (5), or halogen acids (6). In each such case the product possesses more or less active hydrogen in the place of the halogen. Such halogen has accordingly been designated as "positive" (7), this term being used by different authors with varying degrees of literalness. Most of the criteria for "positive" halogen have been qualitative in nature and have suggested a sharp distinction between halogen which was "positive" and halogen which was not. It seems more likely that the replacement of halogen by hydrogen is a mode of reaction which is available in all halogen compounds, but comes to the fore only when the equilibrium, or rate of reaction, or both, is more favorable to it than to other competing reactions.

Our present purpose is to discover the importance of equilibria, rates, and mechanisms in determining the degree of apparent "positivity" of halogen in a series of compounds. The results show that when a reversible reaction is chosen as the basis of comparison of a series of compounds, both the equilibrium and the rate of the reaction are greatly dependent upon structure; that there are at least two mechanisms for establishing the equilibrium, and the relative importance of these two mechanisms also varies with structure. In no case does the mode of reaction characteristic of "positive halogen" disappear, but it may become very slow and the equilibrium may become unfavorable to its occurrence.

The reaction chosen for comparison is that between a bromo compound and hydrogen bromide to give bromine and the debrominated compound, illustrated by the debromination of bromodiphenylacetophenone:



This is a general reaction for α-bromo ketones. The more active the the hydrogen in the parent ketone, broadly speaking, the more rapidly this reaction occurs. It is, moreover, an entirely typical "positive halogen" reaction, in which the bromine of the original organic compound pairs up with the negative part of the attacking reagent. It is free from the usual competing reaction, since an interchange of the bromide ion with the bromine of the ketone would lead to products identical with the starting materials.

Despite the apparent simplicity of this reaction, there were many difficulties in the way of accurate velocity and equilibrium determinations. The results in some individual cases are much more reproducible than in others. Divergences of 50% between determinations of the same quantity by different methods often occur. Nevertheless, the differences between compounds being compared are so large that these rough measurements are capable of yielding useful information, and are accordingly presented.

This debromination reaction is the reverse of the bromination of a ketone, a reaction which has been much studied kinetically in polar solvents (8). Such studies have usually been carried out on ketones and under conditions such that the bromination is practically irreversible Under these conditions the rate of bromination is found to be governed by the rate of formation of the enol and independent of the bromine concentration. For our studies it has been convenient to make the reaction irreversible in the direction of debromination by including a compound which would react with the bromine as fast as it was liberated. Under these conditions the rate is bimolecular, depending upon the concentrations of the bromo ketone and of the hydrogen bromide and independent of the bromine-acceptor. Now, despite the generally recognized fact that at equilibrium a reaction must be proceeding both forward and backward by the same mechanism and with the same rate-determining step, we have here an illustration of the fact that if a forward and reverse reaction are studied separately and under irreversible conditions, they may not have the same rate-determining step and the quotient of the constants determined will not be equal to the equilibrium constant. We have accordingly studied the bromination of diphenylacetophenone in glacial acetic acid containing fourteen equivalents of sodium acetate to prevent its reversal, and the debromination of the resulting bromo ketone in glacial acetic acid containing cyclohexene to consume the bromine. The irreversible bromination is promoted by light, but in the dark proceeds very slowly and at a rate independent of the bromine concentration and not inhibited by antioxidants. This indicates that enolization, an acid-base catalyzed reaction, is the rate-determining step. The irreversible debromination is unaffected by light and by substantial concentrations of

peroxides or antioxidants. It proceeds at a reproducible rate which is proportional to both the hydrogen bromide and bromo ketone concentrations. In the chart of Figure I the equilibrium constant K for the debromination reaction can be seen to be equal to k_2k_4/k_1k_3, whereas under the irreversible conditions of the kinetic measurements only k_1 and k_4 have been determined.

A run conducted without added sodium acetate began very slowly but showed autocatalysis and, after starting, went rapidly to equilibrium. The equilibrium constant for debromination was 0.0015 as determined from this run. This was in rough agreement with values (0.003) determined by approaching the equilibrium from the direction of bromodiphenylacetophenone and hydrogen bromide. It is not certain that the alpha carbon atom is brominated exclusively in this case, but this is rendered highly probable by the fact that in the runs carried out under reversible conditions

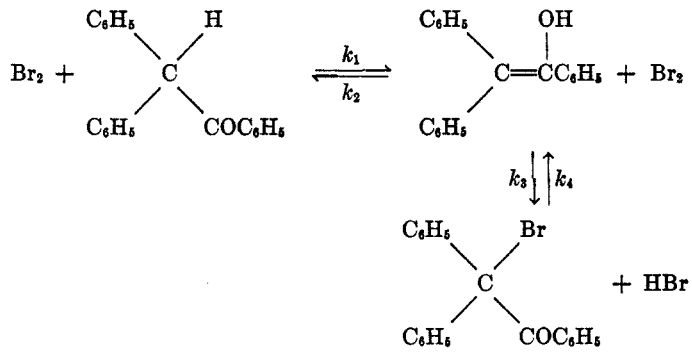


FIGURE I

a constant equilibrium point was reached. Any bromination of the benzene rings would occur irreversibly and result in constantly diminishing bromine concentration rather than an equilibrium. If there is an atomic-chain mechanism for the bromination there must be one also for the debromination. The failure of this to appear under the conditions of our work is doubtless due to the method which we used to ensure irreversibility. The excess cyclohexene which is present in the debrominations must be a very active acceptor for bromine atoms, and must thus serve as an effective inhibitor for the peroxide-catalyzed debromination. When a cyclohexene molecule picks up such a bromine atom in the presence of much hydrogen bromide, it may be expected to start a chain addition of hydrogen bromide to cyclohexene according to the mechanism of Kharasch, Engelmann, and Mayo (9). If these chains are short they will lower the concentrations of cyclohexene and hydrogen bromide by negligible amounts in the process

of inhibiting the chain debromination. Since light requires molecular bromine, and peroxides require hydrogen bromide, in order to produce bromine atoms, the absence of a light effect on the irreversible debrominations and of a peroxide effect on the brominations in the presence of base, is to be expected.

The existence of reproducible rates in each direction in the absence of peroxides shows that there is also a polar mechanism of bromination and debromination, probably identical with that which has been discussed previously for the bromination of enols in polar solvents (10).

Like bromodiphenylacetophenone, the related diketones—methyl-, phenyl-, and benzhydryl- bromodibenzoylmethanes—and bromodi- and bromotri- benzoylmethanes in their irreversible reactions with hydrogen bromide showed no detectable peroxide effect.

Triphenylmethane has weakly active hydrogen, but offers no possibility of an enolic polar mechanism for the establishment of equilibrium in its bromination. It is not surprising to find that triphenylbromomethane shows no reaction with hydrogen bromide in glacial acetic acid in the absence of peroxide, but that added peroxide brings about a liberation of bromine (titer, 1.47 cc. of thiosulfate) in excess of that due to oxidation of the hydrogen bromide by the peroxide (titer, 0.74 cc. of thiosulfate). The reaction is slow at best and the catalyst is used up before equilibrium has been reached. However, by approaching this equilibrium from both directions we were able to find that the equilibrium constant for the debromination of bromotriphenylmethane by hydrogen bromide must lie between the limits 0.015 and 0.043. It is probably very near the latter value, which was the constant limit approached in the bromination of triphenylmethane.

The conversion of alpha- into gamma- bromoacetoacetic ester in the presence of hydrogen bromide is most simply regarded as a reversal of the original bromination to an equilibrium, followed by a slower and less reversible bromination in the new position. Kharasch, Sternfeld, and Mayo (11) have observed that this conversion is dependent upon the presence of peroxide for its occurrence. From our results we should predict that the debromination ought to be capable of occurring by a polar mechanism, since the bromine involved is in the alpha position to two carbonyl groups. The peroxide mechanism would, on the other hand, be expected to be rather important in the rebromination stage at a position at which enolization is probably uncommonly slow.

Table I summarizes the equilibrium and rate constants for the debromination of eight bromo compounds by hydrogen bromide in glacial acetic acid. With the exception of bromobenzhydryldibenzoylmethane and bromotriphenylmethane, all the equilibrium constants have been checked

by approaching the equilibrium from both sides, and a common value obtained. Rate constants have been obtained under antioxidant conditions for the debromination reaction of all but bromotriphenylmethane and triethyl bromomethanetricarboxylate. The progressive replacement of benzoyl groups of bromotribenzoylmethane by phenyl leads to a lowering of both the equilibrium and rate constants for the debromination reaction. The replacement of one benzoyl by methyl has about the same effect as the replacement of two benzoyls by phenyl. Dibenzoylbromomethane has an enormously high rate constant but a rather low equilibrium constant. The latter is intelligible in terms of a high degree of enolization of this bromo ketone, which has very active hydrogen, but this is only an explanation if it is the keto form of the bromo ketone which undergoes debromination, and this renders the high reactivity of the compound the more puz-

TABLE I

EQUILIBRIUM CONSTANTS K AND FORWARD RATE CONSTANTS k_2 (UNDER ANTIOXIDANT CONDITIONS) FOR THE DEBROMINATION OF BROMO COMPOUNDS WITH HYDROGEN BROMIDE IN GLACIAL ACETIC ACID SOLUTION AT 25°

COMPOUND	K	k_2
Bromotribenzoylmethane	2.4	26.
Phenylbromodibenzoylmethane	0.17	11.
Bromodiphenylacetophenone	.003	1.2
Bromotriphenylmethane	.04	.....
Benzhydrylbromodibenzoylmethane	.30	0.65
Methylbromodibenzoylmethane	.0006	0.24
Bromodibenzoylmethane	.01	550.
Triethyl bromomethanetricarboxylate	.075	.....

$$K = \frac{[RH]\,[Br_2]}{[RBr]\,[HBr]}.$$

zling. This bromo ketone cannot, of course, proceed to equilibrium with its debromination product without at the same time establishing equilibrium with dibromodibenzoylmethane. This may influence the apparently displaced equilibrium, in which each atom of organically combined bromine is assumed to be in a molecule of the monobromo compound.

EXPERIMENTAL

Materials

Cyclohexene was fractionally distilled in a slow stream of nitrogen. The fraction used, boiling at 83.2°, was stored under nitrogen, as were the stock solutions in glacial acetic acid made up from it. All these were tested for peroxide with potassium iodide.

The ketones and bromo ketones were prepared and purified by standard methods

in the literature. Table II shows their properties. Bromotribenzoylmethane was prepared as described by Bartlett and Cohen (10) and not by the method of Werner (12), which gives cleavage of the triketone.

The *glacial acetic acid* was purified as follows. The technical product of the Niacet Co. was fractionally distilled through a nine-foot column packed with glass helices at a reflux ratio of 10 to 1. A yield of 63% was obtained of fractions melting sharply at 16.6°. This solvent was used for the equilibrium determinations. Two more batches were prepared with preliminary treatment with chromic anhydride (13), and these samples were used in all the runs in which the control of peroxide content was important.

TABLE II

PURIFICATION OF COMPOUNDS USED FOR MEASUREMENTS

COMPOUND	SOLVENT FOR RECRYSTALLIZATION	M.P., °C.
Dibenzoylmethane	Methanol	75.8–76.8
Bromodibenzoylmethane	Chloroform-ligroin	90.8–91.2
Triphenylmethane	Benzene	92.5–93
Bromotriphenylmethane	Carbon disulfide	151–152
Diphenylacetophenone	Acetic acid	136
Bromodiphenylacetophenone	Pet. ether-chloroform	97.0
Phenyldibenzoylmethane	Ether-pet. ether	147–148
Phenylbromodibenzoylmethane	Methanol	87.5–88.5
Tribenzoylmethane	Acetone	206–210
Bromotribenzoylmethane	Methanol	118–119
Benzhydryldibenzoylmethane	Methanol-acetone	220.5–222
Bromobenzhydryldibenzoylmethane	Methanol-acetone	115.5–116.5
[a]Methyldibenzoylmethane	Ether	82–83
[a]Methylbromodibenzoylmethane	Ethanol-water	64–64.8
Triethyl methanetricarboxylate		(b.p. 150.1–150.2/25 mm.)
Triethyl bromomethanetricarboxylate		(b.p. 154–155 at 13 mm.)

[a] These preparations were made by A. Bavley.

Measurements

In the reactions being studied it is possible either to titrate the bromine by a method which will not affect the bromo ketone or to destroy the bromine quickly, then liberate and titrate the bromine from the bromo ketone. Which method is advantageous depends upon the speed with which the "positive" halogen reacts with hydrogen bromide or hydrogen iodide. We have used altogether four variations of procedure, to which we shall hereafter refer by number.

Method 1. An aliquot portion of the solution was added by pipette to excess cyclohexene in glacial acetic acid under nitrogen, which quickly removed the bromine. To this solution was added solid potassium iodide and the flask was swirled for a time determined to be adequate in the individual case. An aqueous solution of sodium acetate was then added and the iodine was titrated with standard thiosulfate solution in the presence of the precipitated organic material.

Method 2. This is like Method 1 except that the potassium iodide was added in aqueous solution instead of in solid form to the bromine compound in acetic acid. This method was applicable only to the most reactive bromo compounds, but for these it saved a step in the analysis.

Method 3 consisted in the direct determination of bromine by adding the solution to aqueous potassium iodide and partially neutralizing the acetic acid with sodium hydroxide, or adding sodium acetate, then titrating with thiosulfate immediately. This and the following method were applied only to bromo compounds whose reaction with hydrogen iodide was slow.

Method 4. This was used only for rate determinations. A known amount of cyclohexene was used in the run. In each aliquot sample the excess of cyclohexene was determined by reaction with excess bromine and iodimetric back-titration.

Methods 1 and 2 suffered from the disadvantage that a considerable excess of cyclohexene was necessary to make the consumption of the free bromine rapid. Such an excess of cyclohexene, when it contained peroxide, seemed to react to some extent with the iodine liberated in the later step. Method 3 obviously could not be used in the rate runs conducted in the presence of cyclohexene.

Rate of bromination of diphenylacetophenone. The brominations in the presence of sodium acetate were so slow that it was not convenient to carry them to more than a small fraction of completion. Method 3 was used. A typical run in the dark required 432 hours for the bromination of 25% of the ketone. Therefore in all the dark runs the first- and second-order equations fitted equally well, and to determine the order of the reaction it was necessary to compare the values of the unimolecular and bimolecular velocity constants k' and k'' obtained with different concentrations of bromine. For all completely dark runs for which constants are reported the plots of log [ketone] and log $\frac{[\text{ketone}]}{[\text{Br}_2]}$ against time are linear beyond the initial jump. In the runs conducted in the light such plots are not linear, but the time required for attainment of a given fraction of the reaction is so much less than in the dark as to indicate a strong effect of diffuse light. Table III summarizes the runs. Runs 1, 2, 3, and 4 were carried out without the complete exclusion of daylight. The blackened flask of Run 4 was moved into the dark room after 96 hours. Runs 5 to 12 were conducted in the dark room, the solutions being added and samples taken by dim artificial light. The unimolecular constants for the six runs containing sodium acetate vary only from 4.9 to 6.9 $\times 10^{-4}$, whereas the bimolecular constants vary from 1.1 to 3.1 $\times 10^{-2}$ as the initial bromine concentration is changed from 0.0535 to 0.0261. Among these runs giving concordant values of the unimolecular constant are five with access of air and one with an antioxidant. In addition there were two runs without sodium acetate in which the reaction, slow to start, approached equilibrium rapidly when once started. In Run 10 the reaction appeared not to have started after five hours, but at six hours it had reached equilibrium. We might interpret this as meaning either that hydrogen bromide is a powerful catalyst for enolization or that its presence, with undetected peroxide, starts a rapid atomic chain leading to bromination. The latter alternative is less probable, since there was an antioxidant present in Run 10 which should have suppressed the chain reaction.

There was always an initial jump in the unimolecular or bimolecular plot corresponding to the rapid consumption of about 4% of the diphenylacetophenone. From Runs 7 and 8 this rapid consumption appeared to require about two hours, although in most of the runs the first titration was not taken until about five hours had elapsed,

and this and all subsequent points lay on the straight line. This may indicate an enol content of about 4% in a solution of diphenylacetophenone in acetic acid at equilibrium. The magnitude of the jump was independent of the time the solution stood before the bromine was added. If this interpretation of the effect is correct, it is strange that the subsequent enolization rate of the ketone should be so small, either in the presence or absence of sodium acetate. Four per cent of reducing impurity in the ketone is perhaps not out of the question.

Rates of debromination. These runs as well as all others in this paper were conducted in a thermostat at 25°. A freshly prepared solution of weighed bromo compound was brought to temperature in the thermostat. Where Method 1 was to be used for analysis, the solution was evacuated and the air replaced by nitrogen, followed by the introduction of a known amount of standard cyclohexene solution.

TABLE III

SUMMARY OF UNIMOLECULAR (k') AND BIMOLECULAR (k'') CONSTANTS FOR THE BROMINATION OF DIPHENYLACETOPHENONE IN GLACIAL ACETIC ACID AT 25°

RUN	CONDITIONS	[KETONE]	[Br$_2$]	$k' \times 10^4$ (Time in hours)	$k'' \times 10^2$ (Time in hours)	% COMPLETION
1	Daylight	0.0214	0.02384	....	....	33 (46 hrs.)
2	Daylight	.0205	.0496	....	....	65 (120 hrs.)
3	Blackened flask in daylight	.0210	.0503	27.	5.7	23 (103 hrs.)
4	Blackened flask	.0204	.0556	12.5	2.4	40 (331 hrs.)
5	Dark	.0220	.0250	4.9	2.3	28 (572 hrs.)
6	Dark	.0228	.0292	6.2	2.4	21 (287 hrs.)
7	Dark	.0210	.0238	5.7	2.8	25 (432 hrs.)
8	Dark	.0182	.0216	5.3	2.6	10 (68 hrs.)
9	No NaOAc, Dark—Reversible, autocatalytic					
10	No NaOAc, Dark 0.01 mole tetrabromohydroquinone	.0155	.02445	Reversible, autocatalytic		
11	Satd. hexabromodiphenylamine dark	.0173	.0261	6.9	3.1	31 (19 days)
12	Dark	.0216	.0535	5.6	1.1	35 (28 days)

The reaction was started by adding a standard solution of hydrogen bromide in acetic acid from a pipette. The peroxides used were ascaridole and, more often, cyclohexene peroxide. The concentrations of these peroxides were determined before addition of the bromo compound to the solution, by iodometric titration. When cyclohexene peroxide was used it was obtained by using a cyclohexene solution which had been exposed to the air. In all peroxide-free runs the absence of peroxides was confirmed by blank titrations. Tetrabromohydroquinone was used as an antioxidant.

Diphenylbromoacetophenone. Table IV summarizes the runs which were performed with this ketone without peroxide.

In the titration by Method 1 the iodine liberated is the sum of that due to the

bromo ketone and that due to any peroxide present. The latter quantity was determined on blank samples, and with ascaridole good checks were obtained between the observed and calculated amounts of iodine liberated. On a test solution of ascaridole the calculated thiosulfate titer was 3.66 cc. and that found, after 45 minutes with hydrogen bromide and potassium iodide in acetic acid under nitrogen, was 3.70. The entire amount of added ascaridole still appeared to be present after the bromo ketone had completely reacted in the debromination runs.

Run 2, in which a considerably oxidized solution of cyclohexene was used, showed an apparently arrested reaction for which we are unable to account. The solution turned quite dark and the end-points were poor. The same was true of Run 4, carried out with somewhat less of the same cyclohexene-peroxide solution, and which gave a rate constant distinctly lower than the rest.

TABLE IV

RATE OF DEBROMINATION OF DIPHENYLBROMOACETOPHENONE AT 25° IN GLACIAL ACETIC ACID BY HYDROGEN BROMIDE

RUN	$[Br\text{-}KETONE]_0$	$[HBr]_0$	PEROXIDE OR ANTIOXIDANT	MOLE-EQUIV.	k (TIME MIN.)	% COMPLETION
1	0.0113	0.0625	$C_6Br_4(OH)_2$	0.046	1.1	90
2	.0119	.0626	$C_6H_{10}O_2$	.041	No reaction	....
3	.0114	.0616	None		1.2	85
4	.0120	.0656	$C_6H_{10}O_2$	.025	0.9	75
5	.0122	.0656	Ascaridole	.052	1.2	95
6	.0167	.0656	"	.037	1.1	90
7	.0124	.0616	$C_6Br_4(OH)_2$ (in dark)	.042	1.2	95

TABLE V

RATE OF DEBROMINATION OF BROMODIBENZOYLMETHANE BY HYDROGEN BROMIDE IN ACETIC ACID SOLUTION AT 25°

RUN	$[Br\text{-}KETONE]_0$	$[HBr]_0$	CONDITIONS	k'
5	0.0171	0.0212	0.009 m.e. $C_6Br_4(OH)_2$	550
6	.0089	.0089	.027 m.e. "	580
7	.0047	.0058	.033 m.e. cyclohexene peroxide	550

Bromodibenzoylmethane. When the results of Runs 1–4 were plotted as bimolecular reactions, curves of decreasing slope were obtained. This was found to be due to the inability of a low concentration of cyclohexene to remove the bromine fast enough to prevent some reversal of the reaction. This was overcome in the later runs by the use of an excess of cyclohexene, tenfold for Runs 5 and 6. Table V summarizes the results.

In this table "m.e." means mole-equivalents, moles of the inhibitor or peroxide per mole of bromo ketone. The time in the rate constants is expressed in minutes. The data for Runs 1–4 are omitted since no constants could be calculated from them and they were hence uninformative.

Phenylbromodibenzoylmethane. Method 1 was used. The only difficulty encountered in the runs with this bromo ketone was its slow reaction with potassium

iodide. Run 1, in which only thirty minutes was allowed for the decomposition of the samples, gave a curve of decreasing slope when plotted as a bimolecular reaction. By extending the time of decomposition to 4½ hours we obtained straight lines and concordant values of the rate constant from runs having from a threefold (Run 3) to a sevenfold (Run 2) excess of cyclohexene. In the three runs of Table VI the points covered 70, 99, and 90% of the total reaction, respectively, and the bimolecular plots were quite linear.

Benzhydrylbromodibenzoylmethane. Methods 1 and 4 were used in the titration. In both cases an excess of cyclohexene containing a small amount of peroxide introduced an error during the titration which prevented the plots from being linear. This was the case with Runs 1 and 5. The minimum time of standing with the potassium iodide was found to be three hours for complete decomposition of the bromo ketone by Method 1.

TABLE VI

RATE OF DEBROMINATION OF PHENYLBROMODIBENZOYLMETHANE BY HYDROGEN BROMIDE IN ACETIC ACID AT 25°

RUN	[Br-KETONE]$_0$	[HBr]$_0$	CONDITIONS	k' (TIME IN MINUTES)
2	0.0108	0.0192	0.04 m.e. $C_6Br_4(OH)_2$	10.6
3	.0069	.0181	.06 m.e. "	11.1
4[a]	.0086	.0282	No antioxidant	13.7

[a] Run 4 was performed by A. J. Wells, Jr.

TABLE VII

RATE OF DEBROMINATION OF BENZHYDRYLBROMODIBENZOYLMETHANE BY HYDROGEN BROMIDE IN ACETIC ACID AT 25°

RUN	[Br-KETONE]$_0$	[HBr]$_0$	$C_6Br_4(OH)_2$ MOLE-EQUIV.	METHOD	k'
2	0.00812	0.0262	0.052	1	0.5
3	.00366	.1653	None	1	.65
4	.01068	.0973	None	1	.71
6	.00693	.0362	0.06	4	.65

In a single experiment on the bromination of benzhydryldibenzoylmethane there was no rapid immediate consumption of bromine, indicating the absence of any appreciable amount of enol at equilibrium.

Table VII summarizes the results of the runs on the debromination of benzhydrylbromodibenzoylmethane.

Methylbromodibenzoylmethane. Method 4 was used. It was determined in blank tests that the reduced ketone had no disturbing effect on the bromometric titration of cyclohexene, which made it probable that there was no disturbing enol content at equilibrium. Table VIII summarizes the results.

Bromotribenzoylmethane. Method 2 was used, the time for decomposition of a sample being 6–15 minutes. Blank tests showed that the peroxides and antioxidants used did not interfere with the determination of bromo ketone. Table IX sum-

marizes the results of the kinetic runs. These runs usually covered about 90% of the total reaction and within this limit gave satisfactory straight lines when plotted as bimolecular reactions. Although from a solution containing bromotribenzoylmethane and hydrogen bromide the cleavage products, benzoyl bromide and bromodibenzoylmethane, are readily obtained, it has been shown that under the present conditions, in the presence of cyclohexene, this cleavage is avoided and we are in fact measuring the debromination of the bromo ketone (14).

TABLE VIII

RATE OF DEBROMINATION OF METHYLBROMODIBENZOYLMETHANE BY HYDROGEN BROMIDE IN ACETIC ACID AT 25°

RUN	[Br-KETONE]$_0$	MOLE EQUIVALENTS		k'
		Peroxide	$C_6Br_4(OH)_2$	
1	0.00965	0.025	0.038	0.26
2	.00992		.037	.25
3	.01102		None	.22
4	.00826		0.046	.27
5	.00923		None	.24
6	.00985		None	.24

The bimolecular plots were all linear.

TABLE IX

RATE OF DEBROMINATION OF BROMOTRIBENZOYLMETHANE BY HYDROGEN BROMIDE IN ACETIC ACID AT 25°

RUN	[Br-KETONE]$_0$	[HBr]$_0$	MOLE-EQUIVALENTS PEROXIDE OR ANTIOXIDANT		k'
1	0.00675	0.01340	None		26.7
2	.00760	.01202	None		26.1
3	.00780	.0160	$C_6H_5NH_3Cl$	0.34	25.6
4	.00817	.0160	Cyc. peroxide	.043	24.
5	.00779	.0160	$C_6Br_4(OH)_2$	.073	26.5
6	.00905	.02525	None		21.
7	.00621	.0206	$C_6Br_4(OH)_2$	.016	28.2
8	.00659	.0252	Cyc. peroxide	.043	25.
9	.00631	.0062	None		38.
10	.00777	.0253	None		25.

Run 9, which deviates most from the others in the value of the rate constant determined, was carried out with approximately equal concentrations of the reactants. Accordingly, instead of plotting $\log\frac{[HBr]}{[Br\text{-}Ketone]}$ against time, the quantity plotted was the reciprocal of the common concentration of these reactants. This made the rate constant somewhat more sensitive to small errors in the concentrations.

Run 1 was carried out in the dark and the others in the light.

Measurement of equilibrium constants

The experience gained in making the rate determinations served as a guide in the choice of conditions and methods for the equilibrium measurements. In each case a knowledge of the rates involved told us how long to allow for the attainment of equilibrium and what titration method to employ for its measurement. In each case the equilibrium was approached from both sides and measurements were made over a wide enough time interval to confirm the attainment of equilibrium. When Method 1 was used, the amount of added cyclohexene was kept down to the minimum consistent with accurate titration.

No attempt will be made to report all the experiments which were made on equilibrium constants. In many cases samples from the same run were analyzed by slightly different methods in the course of discovering the procedure best adapted to the case at hand. In each case samples were taken at times different enough to ensure

TABLE X

EQUILIBRIUM OF DEBROMINATION OF PHENYLBROMODIBENZOYLMETHANE BY HYDROGEN BROMIDE IN GLACIAL ACETIC ACID AT 25°

TIME, HRS.	$[Br_2] \times 10^3$	[KETONE] $\times 10^3$	$[HBr] \times 10^3$	[Br-KETONE] $\times 10^3$	K
			Run 1		
20.4	0.029	0.156	0.186	0.186	0.13
22.6	.027	.154	.188	.188	.12
23.6	.027	.154	.188	.188	.12
			Run 2		
22.0	.014	.274	.114	.114	.29
24.9	.009	.269	.119	.119	.17
43.4	.011	.271	.117	.117	.22
			Run 3		
17.7	.145	.131	.445	.247	.17
18.2	.142	.128	.448	.250	.16
41.6	.145	.131	.445	.247	.17

the attainment of equilibrium. As illustrative data we report in Table X three runs on phenyldibenzoylmethane. Runs 1 and 2 began with the ketone and bromine, and Run 3 began with bromo ketone and hydrogen bromide. Method 1 was used on all samples, 12–18 minutes being allowed for decomposition of the samples by potassium iodide.

Table XI compares the values of the equilibrium constant obtained from different runs and from the two directions for each bromo ketone. K is, as before, the equilibrium constant for the debromination.

As is obvious from the table, the equilibrium values are not nearly so concordant as the rate values. This would be expected since the determination in most cases depends upon hydrogen iodide reacting much more rapidly than hydrogen bromide with the bromo ketone. In a velocity determination the errors are all in the same direction and tend to compensate for one another.

With benzhydryldibenzoylmethane, an attempt was made to determine the equi-

librium point starting with the ketone and bromine, but the cleavage reaction (14) proved more disturbing in this case than when starting with the bromo ketone and hydrogen bromide.

TABLE XI

EQUILIBRIUM CONSTANTS FOR DEBROMINATION OF BROMO KETONES BY HYDROGEN BROMIDE IN GLACIAL ACETIC ACID AT 25°

KETONE	RUN	EQUILIBRIUM CONSTANT FROM	
		Ketone + Br_2	Br-Ketone + HBr
Phenyldibenzoylmethane	1	0.13	.....
	2	.22	.....
	3		0.17
Diphenylacetophenone	1	.002	.....
	2	.002	.....
	3	.....	.004
	4	.....	.003
Dibenzoylmethane	1	.....	.002
	2	.....	.01
	3	.....	.004
	4	.....	.02
	5	.....	.01
	6	.01	.....
Tribenzoylmethane	1	.....	1.7
	2	.....	2.9
	3	2.5	.....
Benzhydryldibenzoylmethane	1	.....	0.27
	2	.....	.20
	3	.....	.31
Methyldibenzoylmethane	1	0.0007	.....
	2	.....	.0006
Triethyl methanetricarboxylate	1	.....	.070
	2	.080	.....
Triphenylmethane	1	.....	.015
	2	.043	.....

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SUMMARY

Measurements of rate and equilibrium have been made on the debromination of some bromo ketones by hydrogen bromide in glacial acetic acid

solution. This is regarded as a typical reaction of the so-called "positive halogen." The measurements are summarized in Table I.

The establishment of equilibrium in the bromination of diphenylacetophenone is strongly promoted by light. By implication there must be a peroxide-catalyzed mechanism for the reverse reaction, but the special conditions of our measurements prevented its detection. Peroxides are necessary to the reaction between hydrogen bromide and bromotriphenylmethane. However, the compounds having bromine in the α-position to a carbonyl group react with hydrogen bromide at a rate which is independent of the concentration of peroxides or antioxidants (in the presence of cyclohexene) and which is attributable to a polar mechanism, presumably the exact reversal of the bromination of a ketone through its enol in a polar solvent. These peroxide-independent rates are compared in Table I.

Both the equilibrium and rate of the debromination are greatly dependent upon structure, but do not show any general parallelism with each other. The results emphasize that there can be no sharp distinction between "positive" halogen and other halogen. In no case does the mode of reaction characteristic of "positive" halogen disappear, but it may become very slow and the equilibrium may become unfavorable to its occurrence.

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