THE RELATIVE RATES OF CERTAIN IONIC REACTIONS

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In order to account for the failure of many homogeneous reactions to be instantaneous, and also for the high temperature coefficients of such reactions, numerous theories[2] have been advanced, mostly involving "activated molecules." Much of this discussion has been handicapped by lack of direct experimental evidence upon the rates of exceedingly rapid, or so-called "instantaneous" reactions. It has been necessary to confine the study of reaction velocity to reactions of relatively slow rate, in order to have it measurable. Most, if not all, of these slow reactions are probably catalytic in nature.

Recently a technique has been developed[3] for measuring the velocity constants of reactions so fast that they are half complete in 0.001 second. This uses an apparatus for mixing the reacting solutions suddenly, and the extent of reaction is estimated by optical or thermal methods at various cross sections of the discharge tube. Even this method fails for reactions of velocity constant higher than about 10^6, and at high dilutions it is rather limited in scope. From kinetic considerations it can be calculated that if every collision between reacting molecules were effective, the velocity constant would be of the order of 10^{15}. Many ionic reactions may have been considered to be of this type, and so have been called "instantaneous." Probably the majority of them are more rapid than the *experimental* limit indicated above. It is desirable, therefore, to find some method that will ascertain whether the speed of these reactions are all of the same order of magnitude, or whether substantial differences exist; and how these differences are affected by variations in temperature, concentration and solvent. It is the purpose of this paper to describe such a method, applicable to some of these "instantaneous" reactions.

This method consists in making "competition" experiments, by adding to a mixture of two compounds an insufficient amount of a reagent which reacts with both; and by suitable analysis determining the extent of each reaction. From these the ratio of the two velocity constants can be cal-

culated. The method was used in a former investigation[4] to estimate the directive influence of substituents in the benzene ring by their effect upon the rate of bromination of aromatic amino and phenolic compounds in aqueous solution. In that paper two inorganic reactions were included, namely, the reactions of bromine with potassium iodide and with titanous chloride, respectively. This suggested the extension of the method to the reactions of bromine with other reducing agents. Aqueous solutions have been used exclusively, since it was desired to study "ionic" reactions.

It is admitted that there is apparently no relation between the rates of oxidation of these reducing agents and their reducing potentials, or the free-energy changes, which could be estimated from equilibrium data. Thus, for example, if insufficient bromine is added to a mixture of titanous chloride and hydriodic acid, only the former is oxidized, in spite of its much slower rate, because it is a stronger reducing agent. It can be considered that the hydriodic acid is first oxidized, but that the iodine formed is reduced by the titanous chloride. A competition experiment between two such reversible reactions is, therefore, impossible. Nor does the inverse relation, sometimes proposed, hold any better, namely, that velocities of reaction are in inverse order to free-energy changes, since stannous chloride is a much stronger reducing agent than ferrous sulfate, which reacts comparatively slowly.

Since most of the reducing agents employed are oxidized reversibly, it was not in general possible to make them compete against each other. But they could be made to compete with certain organic compounds for bromine satisfactorily, since the organic brominations are irreversible, and since the organic compounds are not usually affected by the oxidation products of the inorganic ones. The organic reactions employed were substitutions of hydrogen by bromine, except in the cases of cinnamic acid and aldehyde, which add bromine to the double bond.

In the competition between two organic compounds,[4] there was no difficulty in obtaining homogeneous mixing before reaction, because a bromide-bromate solution, which reacts only slowly with dilute acid to give bromine, was used, and because the bromic acid did not have a direct effect upon the organic compounds. But if an inorganic reducing agent were used with bromide-bromate solution, it would react with the bromic acid much more quickly than would the hydrobromic acid, and thus receive all the oxidizing effect, and the organic compound none, no bromine having been formed. It is necessary, therefore, to use free bromine solution; and the difficulty arises of obtaining a homogeneous mixture of the reactants, since the reactions are so rapid that they take place at the point of entrance of the bromine water, the bromine perhaps not being properly divided between the competitors. Thus, if Competitor A reacts much more

[4] Francis, Hill and Johnston, THIS JOURNAL, 47, 2211 (1925).

rapidly than B, it would become impoverished in the layer of solution adjacent to the bromine water, and allow Competitor B to obtain more than its just share of the bromine. The error thus introduced would usually be on the side of making the competitors seem too nearly equal in speed, and probably would be slight for well-matched competitors.

Several methods have been used previously to obtain gradual mixing of reacting solutions. One depends upon diffusion toward each other of the reactants through undisturbed distilled water. This would be entirely unsuitable for the present purpose because the two competitors probably would diffuse at different rates, and the one which diffused faster would consume most of the bromine. Another method would involve the diffusion of bromine vapor into the mixture of competitors. Both these methods would be very time-consuming, and not readily quantitative in application. It was suggested that bromine vapor diluted with an inert gas be bubbled through the mixture of competitors. This was tried, but the reaction seemed to take place entirely at the orifice of the delivery tube, so much so that, in cases where a precipitate was formed, the orifice was clogged. Furthermore, since it would be difficult to know exactly how much bromine had been added, it would be necessary to analyze the resulting solution for both competitors. This would seldom be practicable. There was also the possibility that the interaction of bromine and water must precede the reaction with one competitor and not that of the other.

Fig. 1.

With the purpose of minimizing the error due to non-homogeneous mixing, and yet of obtaining positive mixing of definite quantities of the reactants in a reasonable time, a simple apparatus was devised as shown in Fig. 1. This delivered two solutions, the bromine water and the mixture of competitors, at equivalent concentrations, at precisely equal slow rates into a moderate volume of agitated distilled water. If there were enough bromine for both competitors, this would produce the desirable result of a reaction at practically infinite dilution throughout, and yet involve only a small volume of solution; but there would be no competitive effect. In the actual cases studied (with bromine sufficient only for one com-
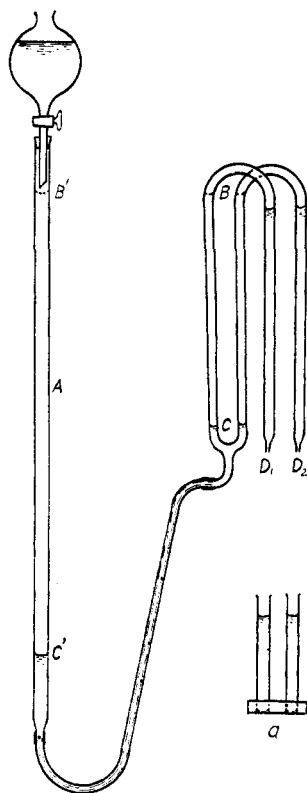
petitor) the error due to non-homogeneous mixture appeared again in the latter part of the mixing; but it can be shown that the total error should be only one-third as great as if only one solution were discharged into the other under corresponding conditions.

The operation of this apparatus was as follows. The two solutions were prepared in two test-tubes with approximately equal volumes, 5 to 10 cc. each, and supported in two holes in a large flat cork stopper (a). The tube A was raised as high as possible (the rest of the apparatus being clamped permanently in position) bringing the water levels up to B; and the cork was raised so that the two delivery tubes D_1 and D_2, were immersed in the solutions. The tube A was then lowered, the water levels falling to C and C' and the solutions being sucked into the delivery tubes, care being taken not to draw in air. A was clamped in place, and a beaker half filled with distilled water or dil. ethanol was supported so that the delivery tubes were immersed in it. Agitation was started, and the test-tubes were rinsed into the beaker. A dropping funnel filled with water was placed in A, and turned on slightly, giving a gentle flow of drops of water. This raised the levels again gradually to B and B', and discharged both solutions into the beaker. About ten minutes was allowed for this except that when there was danger of loss of a volatile compound, such as iodine or sulfur dioxide the mixing and analysis were completed in about four minutes. A final slight raising of A made the water overflow at B, rinsing the delivery tubes into the beaker.

This apparatus was used in most of the competition experiments, but in the case of titanous chloride, which is oxidized easily by atmospheric oxygen, it seemed inapplicable. When this reducing agent was a competitor, the organic compound was dissolved in water or dil. ethanol in a flask, and the air was swept out with a stream of carbon dioxide through a 2-hole stopper. The titanous chloride was added from a buret and then, with vigorous agitation, the bromine water was introduced slowly from a pipet drawn to a fine point. The excess of titanous chloride was estimated by titration with ferric alum, after being heated to boiling, using methylene blue as an indicator.

In all the experiments of this paper, there were taken 1 millimole of the organic compound and sufficient inorganic compound to give two units of reduction, that is, $2TiCl_3$, $2FeSO_4$, etc., but only one $SnCl_2$, $NaHSO_3$, $NaAsO_2$ or $NaNO_2$. In most cases 1 millimole of bromine was used, but with some organic compounds which consume two or more molecular equivalents of bromine, and which reacted more rapidly than the inorganic compound, 2 millimoles of bromine were taken, in order to obtain a better comparison, this still being less than the theoretical requirement. The amount of bromine was considered in the calculation of the results. The "concentrations" given are those which would have existed in the actual

final volumes if the solutions could have been mixed homogeneously before reaction. Those higher than 0.02 N were not obtained with the apparatus of Fig. 1, but in experiments in which the bromine water was added gradually directly to the mixture of competitors. The ratio of the two velocity constants is calculated from the equation,[5]

$$K_{1B}/K_A = \log (1 - x_B)/\log (1 - x_A) \tag{1}$$

in which x_A and x_B are the fractions of the compounds A and B which have reacted (in organic compounds which react with two or more molecular equivalents of bromine, x_B is the fraction of the *primary* reaction, and K_{1B} is the corresponding velocity constant).

Before attempting to estimate the rates of oxidation of the several reducing agents, it seemed best to ascertain the effects of concentration, temperature and solvent, so that the conditions could be chosen intelligently. These observations apply to the cases studied, but cannot as yet be considered of universal application.

Effect of Concentration

In the stoichiometric equation for the interaction of bromine and an organic compound, only a single molecule of the latter appears; but in the reaction for the oxidation by bromine of some of the inorganic compounds, such as titanous chloride or ferrous sulfate, which suffer a valence change of only one unit, two molecules of such compounds appear to take part, if the reaction is written with Br_2 or HOBr. If this represents the conditions, the ratio of rates between titanous chloride and p-toluidine, for example, should vary directly with the concentration, because the reaction with the inorganic compound would be of an order higher by one than that of the organic compound. In all the cases studied, however, the ratio has been found to be nearly independent of concentration. Indeed, if it were not for this fact, it would be nearly hopeless to expect consistent results from this type of experiment, since the actual concentrations during the reaction vary widely.

This observation can be explained by the view previously advanced,[6] namely, that the active agent in aqueous bromination is not hypobromous acid, but nascent bromine, that is, bromine atoms, either uncharged or charged positively. Another possible explanation is that molecular complexes may be formed at first in all cases between bromine and the various competitors. The results are summarized in Table I.

Effect of Temperature

Actual temperature coefficients cannot be found by competition experiments; but differences between those of the competing reactions can be

[5] Ref. 4, p. 2222.

[6] Francis, This Journal, **47**, 2340 (1925). Br^+ also would have two units of oxidizing power, but it can be conceived as being discharged and charged negatively in two steps. There appear to be no analogous concepts for HOBr and Br_2.

TABLE I

EFFECT OF CONCENTRATION UPON THE RATIOS OF VELOCITY CONSTANTS

Competitions for Br$_2$			Temperature 25°		
Competitor A[a]	Competitor B	Concn., N	x_A	x_B	K_{1B}/K_A
Titanous chloride	p-Toluidine	0.1	0.55	0.80	2.1
		.05	.55	.80	2.1
		.05	.47	.83	2.85
		.012	.51	.82	2.35
		.006	.53	.81	2.2
		.005	.56	.79	2.0
Titanous chloride	Cinnamic acid[b]	.05	.72	.28	0.25
		.017	.72	.28	.25
		.006	.68	.32	.35
Titanous chloride	Acetanilide	.10	.39	.61	2.0
		.025	.38	.62	2.1
		.005	.39	.61	2.0
Ferrous sulfate	Acetanilide	.025	.22	.78	6
		.005	.17	.83	9
Ferrous sulfate	Cinnamic acid[b]	.05	.62	.38	0.53
		.025	.60	.40	.57
Hydriodic acid	Resorcinol	.2	.64	.36	.43
		.06	.65	.35	.41
		.018	.64	.36	.44
		.005	.61	.39	.51
Sodium arsenite	Aniline	.04	.56	.59	1.1
		.005	.56	.59	1.1
Potassium ferrocyanide	Aniline	.03	.48	.62	1.5
		.005	.40	.64	2.1
Stannous chloride	m-Cresol	.11	.50	.50	1.0
		.01	.36	.64	2.6
Sodium bisulfite	m-Cresol	.1	.53	.47	0.8
		.01	.50	.50	1.0
Stannous chloride	Sodium bisulfite	.05	.47	.53	1.15
		.006	.47	.53	1.15
				(Competing for I$_2$)	
Sodium bisulfite	Sodium thiosulfate	.05	.44	.56	1.4
		.005	.41	.59	1.8

[a] In all the tables, Competitor A is the one upon which the analysis is based.

[b] Addition of bromine to double bond.

readily estimated, since the observed ratio of rates varies with temperature unless the coefficients are identical. Wide temperature ranges were employed, and the results are presented in Table II. When they are reduced to 10° intervals, the temperature coefficients of all the reactions studied are practically the same. This may mean that these reactions are uncatalyzed and therefore subject perhaps only to kinetic effects, and not to activation of molecules; or it may mean that the reactions have a common catalyst, possibly the hydrogen or hydroxyl portion.[7] The decision would be of

[7] Rice, Fryling and Wesolowski, THIS JOURNAL, **46**, 2407 (1924).

great importance to theory of reaction rate, but it cannot be made from these data. At least, it simplifies the further experiments if the volume and the temperature do not require accurate control.

TABLE II
EFFECT OF TEMPERATURE UPON THE RATIOS OF VELOCITY CONSTANTS
Competitions for Br_2

Competitor A	Competitor B	Concn., N	Temp., °C.	x_A	x_B	K_{1B}/K_A	10° Temp. coef. of ratio
Titanous chloride	p-Toluidine	0.05	25	0.55	0.80	2.1	0.97
		.05	100	.60	.78	1.7	
		.012	25	.51	.82	2.35	.91
		.012	100	.66	.75	1.2	
Titanous chloride	Cinnamic acid	.033	25	.65	.35	0.40	1.0
		.033	100	.66	.34	.39	
Titanous chloride	Acetanilide	.025	25	.38	.62	2.1	0.92
		.025	75	.44	.56	1.4	
		.025	85	.45	.55	1.3	
Ferrous sulfate	Acetanilide	.025	25	.22	.78	6.0	.99
		.025	80	.23	.77	5.5	
Hydriodic acid	Resorcinol	.018	25	.64	.36	0.44	1.1
		.018	45	.60	.40	.54	
Sodium arsenite	Aniline	.005	25	.56	.59	1.12	1.02
		.005	85	.50	.62	1.28	
Potassium ferrocyanide	Aniline	.005	25	.40	.64	2.1	1.02
		.005	80	.38	.65	2.3	
Stannous chloride	m-Cresol	.01	25	.36	.64	2.6	0.99
		.01	70	.37	.63	2.5	
Sodium bisulfite	m-Cresol	.01	25	.50	.51	1.02	.98
		.01	70	.52	.48	0.92	

In order still further to test the effect of temperature upon the relative rates of reaction, a few competition experiments were made between organic

TABLE III
EFFECT OF TEMPERATURE UPON THE RATIOS OF VELOCITY CONSTANTS
Competitions for bromine as $KBr-KBrO_3$

Competitor A	Competitor B	Temp., °C.	z_A or y_A	K_{1B}/K_{1A}	10° Temp. coef. of ratio
Aniline	m-Hydroxybenzoic acid	3	0.323	0.39	0.97
		22	.324	.38	
		42	.333	.35	
		78	.346	.29	
p-Nitrophenol	Cinnamic acid	0	.496	.69	1.02
		0	.510	.64	
		22	.456	.83	
		83	.445	.88	
Aniline	p-Toluidine	8	.742	.154	1.01
		24	.746	.150	
		80	.731	.165	

compounds alone, using bromide-bromate solution. Pairs were chosen with a maximum difference in type of reaction, namely, aniline and *m*-hydroxybenzoic acid (to have one amino and one phenolic compound); *p*-nitrophenol and cinnamic acid (to have one substitution and one addition reaction); and aniline and *p*-toluidine (to have a considerable difference in rate). Table III shows that again the temperature coefficients are the same within experimental error. This is of importance in relation to Skrabel's theory[8] that temperature coefficients are less for more rapid reactions, and approach unity as a limit.

Effect of Solvent

This paper is confined to the study of reactions in aqueous solution, but "aqueous" is not considered to exclude moderately strongly acid or alcoholic solution, provided a substantial proportion of water is present. This interpretation is necessary since most of the organic compounds employed are insoluble in a moderate volume of water, and titanous chloride is hydrolyzed unless the solution is fairly acidic. No organic solvent other than ethanol was used.

It was expected that higher proportions of ethanol might depress the ionization of the inorganic salts, and so perhaps favor the organic compounds in competitions with them. The reverse was observed. When 80 or 85% ethanol was used, the bromine was often consumed almost entirely by the inorganic competitor. With more dilute ethanol the effect was less marked, but in the same direction. In many cases hydrochloric acid had the same influence. The results are summarized in Table IV.

It is, of course, impossible to tell from any one series of competition experiments whether a change in the ratio of rates is due to an acceleration of one reaction or a retardation of the other, or both; or does it greatly matter for the present purpose. A general consideration shows that the results are consistent with the following principle.

The reactivity of a dissolved substance is increased by a change in environment in a direction which would tend to throw it out of solution.

Thus, addition of ethanol decreases the solubility of an inorganic compound and, therefore, increases the degree of saturation of such a solute, while at the same time it increases the solubility of the organic competitor. Both results favor the inorganic reaction. Hydrochloric acid has an analogous effect in the case of the competition between titanous chloride and *p*-toluidine. With titanous chloride and cinnamic acid the opposite is true. The reactivity is thus closely related to thermodynamic activity, which is at a maximum in saturated solution. This is reasonable, but could not have been predicted with certainty. Dimroth[9] discovered this

[8] Skrabel, *Chem.-Ztg.*, **37**, 1169 (1913); *Monatsh.*, **35**, 1230 (1914).

[9] Dimroth, *Ann.*, **377**, 131 (1910).

TABLE IV

EFFECT OF SOLVENT UPON THE RATIO OF VELOCITY CONSTANTS

Competitions for Br_2

Temperature 25°　Concentration uniform in each series

Competitors A and B	Ethanol %[a]	x_A	x_B	K_{1B}/K_A	HCl,[b] %	x_A	x_B	K_{1B}/K_A
Titanous chloride ⎫	0	0.47	0.83	2.85 ⎫	0	0.47	0.83	2.85
⎪	30	.51	.82	2.4 ⎪	11	.50	.82	2.5
⎪	50	.51	.80	1.9 ⎪	20	.66	.75	1.35
p-Toluidine ⎭	75	.71	.74	1.1 ⎭	35	.92	.65	0.03
Titanous chloride ⎫	6	.68	.32	0.35 ⎫	0	.68	.32	0.35
⎪	30	.72	.28	.25 ⎪	6	.68	.32	.35
⎪	35	.72	.28	.25 ⎪	12	.61	.39	.52
Cinnamic acid ⎭	70	.96	.04	.02 ⎭				
Titanous chloride ⎫	0	.38	.62	2.1 ⎫	6	.34	.66	2.5
⎪	40	.73	.27	0.23 ⎬	15	.45	.55	1.3
Acetanilide ⎭	80	1.00	.00	.00 ⎭	30	.92	.08	0.04
Ferrous sulfate ⎫	5	0.22	.78	6 ⎫	0	.22	.78	6
⎪	85	.91	.09	0.04 ⎭	8	.49	.51	1.06
Acetanilide ⎭					30	.93	.07	0.025
Ferrous sulfate ⎫	10	.18	.82	9 ⎫	0	.49	.51	1.04
⎪	25	.37	.63	2 ⎬	5	.55	.45	0.40
Cinnamic acid ⎭	40	.60	.40	0.57 ⎭	10	.77	.23	.18
Hydriodic acid ⎫	0	.64	.36	0.44 ⎫	0	.64	.36	0.44
⎪	60	.71	.29	.27 ⎬	20	.71	.29	.27
Resorcinol ⎭	80	.73	.27	.23 ⎭	30	.73	.27	.23
Sodium arsenite ⎫	0	.56	.59	1.1 ⎫	0	.56	.59	1.1
Aniline ⎭	50	.57	.59	1.1 ⎭	5	.52	.61	1.2
Stannous chloride ⎫	2	.36	.64	2.6 ⎫	0	.36	.64	2.6
m-Cresol ⎭	85	.77	.23	0.19 ⎭	20	.37	.63	2.5
Sodium bisulfite ⎫	2	.50	.51	1.02 ⎫	0	.50	.51	1.02
⎪	70	.56	.44	0.7 ⎬	4	.47	.53	1.2
m-Cresol ⎭	85	.59	.41	.57 ⎭	20	.48	.52	1.09
Stannous chloride ⎫	0	.47	.53	1.15 ⎫	0	.47	.53	1.15
⎪	80	.83	.17	0.11 ⎭	2	.48	.52	1.12
⎪	0	.52	.48	.9 ⎫	0	.52	.48	0.9 (Competing
Sodium bisulfite ⎭	80	.82	.18	.12 ⎭	2	.53	.47	.88　for I_2)
Sodium bisulfite ⎫	0	.41	.59	1.75 ⎫	0	.41	.59	1.75
⎪	80	.06	.94	43 ⎬	0.3	.30	.70	3.5[c] (Competing
Sodium thiosulfate ⎭	85	.04	.96	67 ⎭	1.7	.36	.64	2.3[c]　for I_2)

[a] No hydrochloric acid.　　[b] Minimum amounts of ethanol.

[c] Results uncertain because of decomposition of thiosulfate.

principle as applied to molecular rearrangements.　Bugarsky[10] also mentioned it and referred to van't Hoff[11] for the idea that rates are proportional to active masses.

This principle offers a partial explanation for the high reactivity of certain compounds whose chemical constitutions seem inadequate to explain it.　Thus 2,6-dibromo-aniline has been found to react with bromine 25 times as fast as aniline,[12] although the new bromine atom must enter a position *meta* to two other bromine atoms and, therefore, against their

[10] Bugarsky, Z. physik. Chem., 71, 705 (1910); see especially p. 750.

[11] Van't Hoff, "Lectures on General and Physical Chemistry," Vols. 218-221.

[12] Francis, THIS JOURNAL, 47, 2591 (1925).

influence. This compound is very difficultly soluble in aqueous solution, requiring considerable ethanol and acid, which would cause a relative decrease in the reactivities of its organic competitors. Diphenylamine, which is even more difficultly soluble, is still more reactive. Chemical effects will, of course, usually predominate, but this principle, if it could be applied properly, might modify some conclusions that have been drawn in regard to reactivity. It will be considered in discussing the results of competition experiments between organic compounds in a later paper. No claim is made that this principle is a complete explanation of the effect of solvent upon reaction velocity.

The question arises, what solvent shall be used for the organic competitors, which vary greatly in solubility, in order to obtain consistency throughout the series? Largely for convenience, it was decided to use the minimum portion of ethanol, in each case, which would maintain the substance in solution. This was somewhat arbitrary, but it seemed probable that the reactivity of the compound on the threshold of the solid state would thus be measured, and this was more readily reproduced. Moreover, the reactivity in that region of conditions appeared to be less sensitive to environment than in any other.

Reliability of the Method

In order to establish the reality of the reactivities of the various compounds as measured by competition experiments, it was thought best to carry out two series of experiments in which two inorganic competitors were compared with as many of the same organic compounds as possible. On dividing the ratios obtained in one series by the corresponding ones in the other, the quotients should be the same, that is, the ratio of the reactivities of the two inorganic compounds. Titanous chloride and ferrous sulfate were chosen for this purpose. Table V gives the results, using 25 different organic compounds. The fifth column is obtained by dividing the values in the second by those in the third (not the reverse, since the constants of titanous chloride and ferrous sulfate are denominators in those ratios), and the results are as consistent as could be expected from this type of experiment. The geometric mean rather than the arithmetic mean was taken, in order to give equal weights to divergencies in both directions.

The table includes also the ratios obtained with ferrous chloride in competition with the same series of organic compounds. As was to be expected, the values are the same as for ferrous sulfate, showing that only the ferrous ion takes part in the reaction.

Reactivities of Inorganic Compounds

We are now in a position to estimate the reactivities of several inorganic reducing agents. For this purpose there was used a table of velocity constants of bromination of organic compounds similar to that appearing in

TABLE V

COMPETITIONS FOR BROMINE OF ORGANIC COMPOUNDS WITH TITANOUS CHLORIDE AND
WITH FERROUS SULFATE AND CHLORIDE, RESPECTIVELY

Concentration, about 0.02 N Temperature, 25°   Minimum amounts of ethanol

| Organic competitor | Ratio of constant to that of | | | Ratio FeSO₄/TiCl₃ | Ratio FeSO₄/FeCl₂ |
	TiCl₃	FeSO₄	FeCl₂		
p-Phenolsulfonic acid......	3.0	9.3	10	0.32	1.08
p-Aminophenylacetic acid.	2.2	9	11	.24	1.2
p-Toluidine..............	2.35	5.1	5.6	.46	1.1
1,2-Xylidine-4..........	2.1	4.8	4.3	.43	0.9
Thiocarbanilide..........	1.8	7	6.6	.26	0.94
Acetanilide..............	1.6	5.1	5.4	.31	1.05
Diethylaniline...........	1.66	4.8	5.2	.35	1.08
Dimethylaniline..........	0.99	3.3	3.0	.30	0.91
p-Cresotinic acid........	.84	2.4	2.4	.35	1.0
Formanilide.............	.61	2.8	2.9	.22	1.04
Methyl salicylate........	.50	1.75	1.9	.28	1.08
Cinnamic acid...........	.40	1.3	1.2	.31	0.93
Ethyl salicylate.........	.25	1.2	1.2	.21	1.0
Phenol-disulfonic acid.....	.32	0.9	0.9	.36	1.0
Cinnamic aldehyde.......	.16	.6	.7	.27	1.17
Phenyl-acetanilide........	.13	.48	.45	.27	0.94
Acetyl-o-toluidine........	.14	.46	.5	.30	1.08
Phenacetin..............	.12	.38	.4	.32	1.05
Acetyl-p-toluidine........	.13	.35	.35	.37	1.0
Phenyl salicylate.........	.09	.28	.24	.32	0.86
Bromo-acetanilide........	.05	.25	.24	.20	.96
Diphenyl-guanidine.......	.04	.22	.21	.18	.96
Benzanilide.............	.043	.13	.11	.33	.85
Methyl cinnamate........	.07	.12	.11	.58	.92
Triphenyl-guanidine......	.027	.10	.11	.27	1.1
Geometric mean				0.30	1.01

a former paper,[13] but much more extensive. This will be published in a later communication. The accuracy of the velocity constants of the inorganic reactions is not, however, greatly dependent upon that of the table employed, since comparative values for any two reducing agents were obtained as in the preceding section, using as many as possible of the same organic compounds in competition with each of them. The consistency of the values obtained was considered as a criterion of the reliability of the method, and of the freedom from side reactions and irregular catalytic influences.

The ratios found in this way were not, however, always consistent with the results of competitions between two organic compounds, an observation for which there are three possible explanations. (1) Since phenols, as compared with amino compounds, were uniformly less reactive when

[13] Ref. 4, p. 2228.

competing with reducing agents than when competing directly with amino compounds, it may be that the intermediate -OBr compounds, postulated previously,[14] are partly reduced by the reducing agents before they can rearrange to bromophenols, whereas the corresponding -NHBr or -NBr₂ compounds rearrange much more quickly. (2) The same observation can be explained by the fact that considerable acid was present in the bromide-bromate competitions and very little in the bromine water experiments. The stronger acid would increase the reactivity of phenols and decrease that of amino compounds. (3) Suppose two organic compounds, A and B, are equally reactive chemically, but that A is much less soluble in water than B, so that a moderate concentration of ethanol is necessary to keep it in solution. In direct competition with B it will be much nearer saturation and will, according to the principle mentioned above, react much faster than B; but in competitions with the same inorganic compound, C, only a minimum amount of ethanol is used in each case, so that both A and B are near saturation, and react with equal speed, while the reactivity of C is increased by the greater concentration of ethanol in the former case, and makes A seem by comparison *less* reactive than B. The observed inconsistencies were mostly in the direction indicated by this reasoning; but the effects upon the results of this paper were canceled out entirely by the fact that different reducing agents were used with the same organic compounds under identical conditions.

In many cases the velocity constant of the organic compound was known only very approximately because certain physical characteristics, for example, gummy precipitates, had rendered analysis of the results of the competitions with other organic compounds very difficult. The competitions in the present investigation are not subject to these difficulties, however, since the analyses are all volumetric. In such cases, therefore, the velocity constants of the organic compounds can be estimated most accurately by these experiments. Indeed, this was a primary reason for the present investigation, since the author is engaged principally in researches on directive influence in the benzene ring. A further reason was to ascertain the degree of significance to be ascribed to the results of the organic competitions.

Methods of Analysis

Considerable attention was paid to analytical procedures, and in some cases new methods were devised. In the competitions between two organic compounds gravimetric methods had been used, the highest brominated product of one competitor being separated and weighed, and the results calculated from the partial bromination relations of that compound as found by special experiments.[15] This method was inapplicable in this

[14] (a) Ref. 4, p. 2230. (b) Francis and Hill, THIS JOURNAL, **46**, 2503 (1924).
[15] Ref. 4, p. 2223.

investigation, since it was found to be impossible to obtain good partial bromination curves using free bromine water. The error was due to non-homogeneous mixing and was not corrected in this respect by the apparatus of Fig. 1. The distinction between homogeneous bromination of a mixture of two compounds and homogeneous bromination of a single compound in several stages is analogous to that between the explosibility of gun powder and that of trinitrotoluene, in which the oxygen for combustion is contained in the same molecule. It is true that the extent of the primary stage of the organic bromination (which was necessary in the calculation of the rates) had to be estimated from the total bromine going to the organic compound by some partial bromination scheme, and it was assumed that the one employed previously was followed in these cases also; but the error introduced by this assumption was much less than if the analysis were based upon the weight of the precipitate.

It was very desirable to have a rapid volumetric method of analysis either for the unchanged inorganic reducing agent or for its oxidation product. The methods adopted for the various competitors were as follows.

Hydriodic Acid.—The iodine produced was titrated with sodium thiosulfate solution.

Ferrous Sulfate and Chloride.—The resulting ferric salt was titrated hot with titanous chloride in an atmosphere of carbon dioxide.

Titanous Chloride.—The unchanged compound was titrated hot with ferric alum solution in an atmosphere of carbon dioxide.

Sodium Bisulfite and Stannous Chloride.—The unchanged compounds were titrated with iodine solution.

Potassium Ferrocyanide.—The ferricyanide produced was estimated[16] by adding potassium iodide and zinc sulfate and titrating the resulting iodine with sodium thiosulfate solution.

Sodium Arsenite.—The arsenic acid formed was estimated by boiling with an excess of titanous chloride in an atmosphere of carbon dioxide, followed by titration of the excess with ferric alum solution. The quinquivalent arsenic was reduced quantitatively back to tervalent arsenic. This method was tested with known mixtures and gave good results which are illustrated in Table VI. The procedure was identical with that for

TABLE VI

VOLUMETRIC ANALYSIS OF ARSENIC ACID

Na$_2$HAsO$_4$ Mmoles	NaAsO$_2$ Mmoles	Net TiCl$_3$ Cc.	Quinquivalent arsenic, %	
			Found	Calcd.
1	0	18.74	99.8	100
1	0	18.77	100	100
1	0.5	18.48	65.3	66.7
1	0.5	18.64	66.4	66.7
1	1	18.51	49.1	50.0
0.5	1	9.91	33.6	33.3
0	1	0.01	0	0

[16] Müller and Diefenthäler, Z. anorg. Chem., **67**, 418 (1910).

nitro compounds[17] except that because of the more difficult reducibility of arsenic acid, at least ten minutes' boiling with a considerable excess of titanous chloride was necessary. The iodimetric method, which is satisfactory with arsenic salts alone, could not be used, because in the faintly alkaline solution necessary for quantitative oxidation of the arsenic, some of the organic compounds were iodated.

Sodium Nitrite.—The mixture of nitrite and nitrate was reduced with titanous chloride to nitrous oxide, nitrite consuming two equivalents and nitrate four. This analysis was only approximate, but sufficed in the few competitions which could be made with nitrite, to show that it is oxidized much more slowly than any of the other compounds.

Acid permanganate solution, which was useful in standardizing solutions of several of the above-mentioned compounds, could not be used in the actual analyses, because it oxidized the organic compounds also.

Attempts to include sodium thiosulfate as a competitor for bromine failed because, although its reaction with bromine is substantially the same as that with iodine,[18] provided bromine is not in excess, there was always some decomposition to sulfur and sulfite, which requires twice as much iodine as the thiosulfate from which it was formed, and so interferes with the analysis. A direct competition between thiosulfate and bisulfite for iodine using the apparatus of Fig. 1 was possible, however, and the results are given in Table VII. In these experiments the sulfate produced from the bisulfite was estimated gravimetrically with barium chloride in hydrochloric acid solution, the precipitate being ignited gently to remove sulfur. Thiosulfate is shown to react more quickly with iodine than does bisulfite, a conclusion contrary to that of Eggert.[19] In his experiments he had present only a trace of thiosulfate, and the generality of his conclusion seems open to question.

TABLE VII

COMPETITIONS BETWEEN SODIUM BISULFITE AND SODIUM THIOSULFATE FOR IODINE

Two millimoles of $NaHSO_3$ (A), four of $Na_2S_2O_3$ (B) and two of I_2 in each experiment

BaSO₄ obtd., g.	x_A	K_B/K_A	Remarks
0.2047	0.44	1.4	Mixed suddenly
.1900	.41	1.7	App. of Fig. 1
.1746	.37	2.1	App. of Fig. 1
.2098	.45	1.3	App. of Fig. 1
.1796	.385	2.0	App. of Fig. 1
Mean 0.41		1.7	
0.1890	0.405	1.75	0.03 N NaOH
.0291	.062	43	80% Ethanol
.0209	.045	67	85% Ethanol

The competition for iodine is comparable with that for bromine, the results indicating, probably, the true relative reactivities of the competitors.

[17] Ref. 14 b, p. 2504.

[18] Treadwell and Hall, "Analytical Chemistry, Qualitative Analysis," John Wiley and Sons, 5th ed., 1921, vol. I, pp. 325, 415.

[19] Eggert, Z. Elektrochem., 30, 501 (1924).

This is shown by the experiments with sodium bisulfite and stannous chloride as competitors for both bromine and iodine, the results, which are given in Table VIII, being practically the same in the two cases. The solution was boiled in an atmosphere of carbon dioxide, to remove sulfur dioxide, and cooled, before the iodine titration. This is the only pair where this type of comparison seemed to be possible.

TABLE VIII

COMPETITIONS BETWEEN STANNOUS CHLORIDE AND SODIUM BISULFITE FOR BROMINE AND FOR IODINE

One millimole each of $SnCl_2$ (A), $NaHSO_3$ (B), and halogen. Temperature 25°

Halogen	Volume, cc.	x_A	K_B/K_A	Remarks
Br_2	20	0.47	1.15	
I_2	20	.47	1.15	
I_2	20	.52	0.88	
Br_2	100	.47	1.15	
I_2	100	.52	0.90	
Br_2	100	.48	1.12	2% HCl
I_2	100	.52	0.89	2% HCl
Br_2	50	.82	.11	80% Ethanol
I_2	50	.81	.12	80% Ethanol

Results of the other organic-inorganic competitions are presented in Table IX. Each observed ratio is the mean of at least two closely agreeing results, the average difference being about 3% in the value of x_A, the fraction of the reducing agent which has been oxidized. Many other experiments than those shown were made, but they are not included in the tables because the organic compounds used had been in competition with only a single reducing agent, and so furnish no basis of comparison in this paper.

TABLE IX

THE COMPETITION FOR BROMINE OF INORGANIC REDUCING AGENTS WITH VARIOUS ORGANIC COMPOUNDS

Concentration, about 0.02 N. Temperature, 25°. Minimum amounts of ethanol.

TITANOUS CHLORIDE, POTASSIUM FERROCYANIDE AND SODIUM ARSENITE

Organic competitor	Ratio of constant to that of			Ratios		
	$TiCl_3$	$K_4Fe(CN)_6$	$NaAsO_2$	$\dfrac{K_4Fe(CN)_6}{TiCl_3}$	$\dfrac{NaAsO_2}{K_4Fe(CN)_6}$	$\dfrac{NaAsO_2}{TiCl_3}$
p-Chloro-aniline..........	6.8	1.7	1.32	4.0	1.3	5.15
Metanilic acid...........	5.3	1.1	0.93	4.8	1.2	5.7
m-Aminobenzoic acid.....	5.3	1.6	.92	3.3	1.75	5.7
p-Hydroxybenzaldehyde...	3.6	1.8	.86	2.0	2.1	4.2
p-Toluidine..............	2.85	2.0	.75	1.4	2.6	3.8
Ethylmetanilic acid.......	2.9	1.45	.8	2.0	1.8	3.6
m-Hydroxybenzoic acid...	2.1	1.5	.9	1.4	1.7	2.3
p-Aminophenylacetic acid.	2.2	1.1	.9	2.0	1.2	2.5
				Mean 2.4	1.7	4.0

TABLE IX (*Continued*)

SODIUM BISULFITE AND STANNOUS CHLORIDE

| Organic competitor | Ratio of constant to that of | | NaHSO₃/SnCl₂ |
	NaHSO₃	SnCl₂	NaHSO₃/SnCl₂
Methylaniline....................	1.1	3.2	2.9
o-Toluidine......................	1.16	2.6	2.2
o-Chloro-aniline.................	1.2	2.5	2.1
p-Cresol........................	1.02	2.6	2.5
Anthranilic acid..................	1.03	2.2	2.1
p-Chloro-aniline.................	1.0	1.4	1.4
m-Bromo-aniline.................	0.77	1.7	2.2
m-Toluidine.....................	.84	1.45	1.7
m-Chloro-aniline................	.69	1.6	2.3
Aniline..........................	.65	1.22	1.9
o-Cresol........................	.64	1.15	1.7
p-Cresol........................	.48	0.92	1.9
p-Toluidine.....................	.4	.75	1.9

Mean 2.1

STANNOUS CHLORIDE AND SODIUM ARSENITE

| Organic competitor | Ratio of constant to that of | | Ratio SnCl₂/NaAsO₂ |
	SnCl₂	NaAsO₂	Ratio SnCl₂/NaAsO₂
p-Aminobenzoic acid.............	1.6	1.7	1.06
p-Chloro-aniline.................	1.4	1.32	0.94
m-Bromo-aniline.................	1.37	1.2	.87
m-Chloro-aniline................	1.3	1.2	.92
Aniline..........................	1.25	1.12	.90
o-Cresol........................	1.15	1.4	1.22
2,4-Dichloro-aniline..............	1.0	1.0	1.0
2,4-Dibromo-aniline..............	0.83	1.2	1.4
p-Cresol........................	.92	1.0	1.09
p-Toluidine.....................	.75	0.75	1.0
Acetanilide......................	.41	.4	0.98

Mean 1.02

HYDRIODIC ACID AND SODIUM BISULFITE

| Organic competitor | Ratio of constant to that of | | Ratio HI/NaHSO₃ |
	HI	NaHSO₃	Ratio HI/NaHSO₃
Methylaniline....................	0.96	1.1	1.15
o-Chloro-aniline.................	.68	1.2	1.8
o-Toluidine.....................	.60	1.16	1.9
p-Chloro-aniline.................	.49	1.0	2.0
m-Toluidine.....................	.485	0.84	1.7
m-Bromo-aniline.................	.49	.77	1.6
m-Chloro-aniline................	.50	.69	1.38
Aniline..........................	.43	.65	1.5

Mean 1.6

TABLE IX   (Concluded)

SODIUM NITRITE AND FERROUS SULFATE

Organic competitor	Ratio of constant to that of		Ratio $NaNO_2/FeSO_4$
	$NaNO_3$	$FeSO_4$	
Triphenyl-guanidine................	14	0.1	0.007
Methyl cinnamate (addition)........	10	.12	.012

Mean 0.009

The ratios in these tables are not all quite as consistent as those in Table V, probably because these compounds are more sensitive to environment than are titanous chloride and ferrous salts.   Potassium ferrocyanide, for example, has so high a molecular weight that high weight concentrations must be used, and its difficult solubility in dil. ethanol makes irregularities certain to appear.   Indeed, its higher reactivity than that of ferrous sulfate may be due solely to this fact, in accordance with the principle mentioned above in regard to effect of solvent upon reaction velocity.   Sodium bisulfite was subject to the risk of slight losses of sulfur dioxide during the reaction, and stannous chloride of partial hydrolysis.

The velocity constant of oxidation of titanous chloride by bromine was calculated from those of its organic competitors in more than 100 experiments, including those of Table V, as 0.077 times K_1-aniline, which is of the order[13] of 10^8, the minute being the unit of time. K-$TiCl_3$ is taken as unity as a standard.   By successive employment of the various ratios derived in the preceding tables, the constants of Table X were estimated.

TABLE X

RELATIVE VELOCITY CONSTANTS OF INORGANIC REDUCING AGENTS WITH BROMINE Compared to K-$TiCl_3$

Comp. K.	$Na_2S_2O_3$[a]	HI	$NaHSO_3$	$SnCl_2$	$NaAsO_2$	$K_4Fe(CN)_6$	$TiCl_3$	$FeSO_4$	$FeCl_2$	$NaNO_2$
	15	14	8.6	4.1	4.0	2.4	1.0	0.3	0.3	0.003

[a] Compared with $NaHSO_3$ by competition for I_2.

Many other reducing agents might have been studied, but the list given includes a considerable variety of types.   The significant fact is that these ionic reactions have fairly definite velocity constants, which vary greatly among themselves.   It is possible that a technique could be developed for studying the velocities of other types of ionic reactions and, if this were done, it is probable that analogous conclusions would result.   It may be that Table X has a significance which is not yet apparent.   The various rates of the ionic reactions may be due to the fact that collisions between molecules are effective only when definite portions of their surfaces are in contact.[20]   This idea is not satisfactory for homogeneous reactions in general, however, since the slow ones are probably catalytic.

[20] Stern, Ann. Physik, 44, 497 (1914).   Dushman, THIS JOURNAL, 43, 431 (1921). Bjerrum, Z. physik. Chem.. 108, 87 (1924).

The author is greatly indebted to Professor F. O. Rice of the Johns Hopkins University, who suggested this investigation.

Summary

1. A technique has been developed for measuring the relative rates of certain ionic reactions, namely, the oxidation of some inorganic reducing agents by bromine in aqueous solution. This consists in making these reactions compete with certain irreversible organic substitution reactions.

2. The ratios between the rates of the inorganic and the organic reactions are practically independent of temperature and of concentration.

3. By changing the solvent it is shown that the reactivity of a solute is increased by a decrease in solubility and, like thermodynamic activity, is at a maximum in saturated solution.

4. Ten inorganic compounds have been studied, and shown to have definite velocity constants for oxidation by bromine in aqueous solution, varying in magnitude from 10^4 to 10^8.

5. A new and convenient method for the volumetric analysis of arsenic acid has been found.

6. Sodium·thiosulfate reacts more quickly with iodine than does sodium bisulfite.

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A COLORIMETRIC METHOD FOR THE ESTIMATION OF HYDROXYLAMINE

BY GEORGE W. PUCHER AND HAROLD A. DAY

The procedure reported in this paper is based on the reaction of hydroxylamine with benzoyl chloride and ferric chloride described by Bamberger[1] in 1895. This reaction, as indicated by the literature available from 1907–1925, although used qualitatively, has not been applied to the quantitative analysis of hydroxylamine.

Experimental Part

Standard Solutions and Reagents.—The hydroxylamine hydrochloride used in this work was prepared according to the procedure of Semon.[2] The crude salt so obtained is recrystallized from one-half of its weight of hot water and dehydrated by thoroughly drying in a desic-

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[1] Bamberger, *Ber.*, **32**, 1805 (1895).

[2] Semon, THIS JOURNAL, **45**, 188 (1923).