

Summary

1. The rates of the irreversible oxidation of 1,2- and 1,4-aminophenol and 1,2- and 1,4-aminonaphthol have been studied using reversible reagents of definite potential. The rate is independent of the dilution and is related to the oxidation-reduction potential of the reagent employed.

2. We have suggested that the irreversible oxidation of aminophenols or aminonaphthols proceeds through the reversible formation of the quinone-imine which then irreversibly hydrolyzes. This mechanism is made probable by the evidence which we have obtained of the reversibility of the aminophenol—quinone-imine system in alkaline solutions. The oxidation-reduction potential of this unstable system may be estimated in certain buffer solutions both by the method of mixtures and by titration.

3. The relative rates of oxidation of each amino compound with several reagents of different potentials have been measured and found to be of the order of magnitude predicted from the electrochemical equations which we have developed.

4. It appears that these examples of irreversible oxidation may be formulated in electrochemical terms. This we have done by determining the rates of oxidation of each compound by each member of a graded series of reagents and estimating the potential of the oxidizing agent which should just cause "appreciable oxidation." The potential of this hypothetical reagent (with an oxidizing power of one equivalent) we have defined as the apparent oxidation potential of the substance under investigation.

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THE REACTIVITIES OF SOME TERTIARY BROMIDES

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The work here reported was undertaken with the idea of comparing the reactivities of the halogen atoms in the compounds $(C_6H_5)_3CBr$ (I), $(C_6H_5)_2CBr(CO_2CH_3)$ (II), $(C_6H_5)CBr(CO_2CH_3)_2$ (III) and $CBr(CO_2CH_3)_3$ (IV). These compounds have a certain structural similarity: they may

all be represented by the formula $\begin{matrix} A \\ \diagdown \diagup \\ C > B \end{matrix} CBr$. The phenyl and carb-

alkoxy groups are both negative, and both are activating groups in the sense that they increase the reactivity of methyl halide when they replace one of its hydrogen atoms. From the data presented in recent papers by Conant and his students¹ it appears that the activating influence of the

¹ Conant and Kirner, *THIS JOURNAL*, **46**, 232 (1924). Conant and Hussey, *ibid.*, **47**, 476 (1925). Conant, Kirner and Hussey, *ibid.*, **47**, 488, 587 (1925).

carbethoxy group is much greater than that of phenyl. Thus the relative reactivities of benzyl chloride and ethyl chloro-acetate toward potassium iodide are 197:1720. The reactivity of diphenylchloromethane is not given, but chloromalonic ester is more reactive than triphenylchloromethane. One might thus be led to predict that the order of reactivity of the above-mentioned compounds would be IV>III>II>I.

That this should be true seemed in advance rather improbable. Triphenylbromomethane is a very reactive substance. In certain solvents it shows considerable conductivity² and many of its reactions appear to be ionic. The substances II, III and IV have not hitherto been prepared in a state of purity, but the meager data available on analogous or homologous compounds provide little support for the above prediction.

Attempts to obtain quantitative data on the reactivities of the compounds I-IV have so far been unsuccessful, but a description of their preparation and their qualitative behavior toward certain reagents may be of some interest.

This qualitative behavior is summarized in Table I.

TABLE I
RELATIVE REACTIVITIES OF THE BROMIDES

Substance (C ₆ H ₅) ₃ CBr	Reagents		
	0.1 N AgNO ₃ in abs. CH ₃ CN at room temperature	Abs. CH ₂ OH	KSCN in abs. acetone at room temperature
(C ₆ H ₅) ₃ CBr	Instantaneous ppt.	Instantaneous reaction in cold	Immediate copious ppt. of KBr
(C ₆ H ₅) ₂ CBr(COOCH ₃)	Very rapid ppt.	Reaction 50% complete in 15 minutes at room tem- perature	Slight ppt. in 5 hrs.
(C ₆ H ₅)CBr(COOCH ₃) ₂	Slight ppt. in one week	Action of boiling NaOCH ₃ rapid	Slight ppt. in 5 hrs. (Some decomposition)
CBr(COOCH ₃) ₃	No. ppt. in 3 months	Action of boiling NaOCH ₃ very slow	Slight ppt. in one hr. (Some decomposition)

The order of the reactivities of the substances toward silver nitrate and toward methyl alcohol is I>II>III>IV, the reverse of the predicted order. The unusual inertness of bromotricarbomethoxymethane (IV) is especially noteworthy. It resembles an aromatic halide in its behavior toward these two reagents. A small sample of this ester heated for 14 hours at 110° with an excess of 0.5 N sodium methylate solution gave up only 79% of its bromine. It may be mentioned also that the product of the action of boiling sodium methylate on bromophenylmalonic ester (III) is not the corresponding ether as might be expected, but instead the methyl ether of methyl mandelate: (C₆H₅)CBr(COOCH₃)₂ + CH₃OH → (C₆H₅)CH(OCH₃)(COOCH₃) + CO(OCH₃)₂. Dimethyl carbonate is presumably eliminated in the process.³ The action of sodium methylate on

² Hantzsch and Meyer, *Ber.*, **43**, 336 (1910). Walden, *Z. physik. Chem.*, **43**, 457 (1903). Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 13 (1910). Gomberg, *Ber.*, **35**, 2397 (1902). Hantzsch, *Ber.*, **54**, 2602 (1921).

³ Compare Souther, *THIS JOURNAL*, **46**, 1301 (1924).

methyl diphenylbromo-acetate follows the normal course and the corresponding ether is readily isolated.

The behavior of the substances toward potassium thiocyanate leads to a different conclusion as to their relative reactivities, namely, $I > IV > II > III$. This result is rather surprising in view of the extraordinary inertness of IV toward silver nitrate and toward sodium methylate. I, II and III, however, show the same order of reactivity as with silver nitrate and methyl alcohol.

The behavior of triphenylbromomethane, ethyl diphenylchloro-acetate, diethyl phenylbromomalonate and bromotricarbo-ethoxymethane toward potassium thiocyanate in alcohol has been studied by Wheeler and Johnson,⁴ who showed that all of these compounds react, and that the product is probably in each case (except with bromotricarbo-ethoxymethane) the normal thiocyano compound. When acetone is used as a solvent, the isolation of crystalline thiocyano compounds from the mixture formed by the action of potassium thiocyanate on triphenylbromomethane (I), or on methyl diphenylbromo-acetate (II) presents no difficulty, but with the compounds III and IV a yellow amorphous precipitate which Wheeler and Johnson refer to as pseudothiocyano-gen sulfide separates with the potassium bromide, and attempts to isolate crystalline thiocyano compounds were unsuccessful. The reaction evidently proceeds with decomposition. Nevertheless, the precipitate which separates during the early stages of the reaction was found on analysis to be, in spite of its yellow color, nearly pure potassium bromide; this seems to indicate that the first reaction is a simple double decomposition, and that the formation of the pseudothiocyano-gen sulfide is due to a subsequent reaction. If this is true, the rate of formation of the precipitate should furnish a rough index of the reactivity of the halide toward potassium thiocyanate.

The qualitative behavior described above indicates that triphenylbromomethane is the most reactive member of the series of compounds regardless of the reagent used and that usually the order of reactivity is just the reverse of that which was inferred from the behavior of analogous primary and secondary halides. It is evident that the activating effect of three substituent groups in a methyl halide cannot be predicted from the known effect of one or two such groups. These conclusions receive further support from data already present in the literature. Werner showed some years ago⁵ that tribenzoylmethyl bromide is not affected by boiling alcohol, whereas triphenylmethyl bromide reacts very rapidly with cold alcohol. As Werner pointed out, this is just the reverse of what might be expected from the fact that benzoyl is a more negative group than phenyl. But it is also the reverse of what might be expected from

⁴ Wheeler and Johnson, *THIS JOURNAL*, **24**, 680 (1902).

⁵ Werner, *Ber.*, **39**, 1283 (1906).

the fact that phenacyl chloride, $C_6H_5COCH_2Cl$, is enormously more reactive toward potassium iodide than is benzyl chloride, $C_6H_5CH_2Cl$.⁶

It is evident that the behavior of tertiary halides in general presents some peculiarities and anomalies. The facts presented above seem to show that the accumulation of three mildly activating groups may in one case result in a methyl halide having an extremely high reactivity, whereas the accumulation of three strongly activating groups may in another case result in a methyl halide having an extremely low reactivity. The relative orders of reactivity may also change in a remarkable fashion with the change of reagent. This was referred to in connection with the behavior of the substances toward potassium thiocyanate. In further illustration it may be added that *tert.*-butyl bromide reacts almost instantaneously with silver nitrate in absolute acetonitrile and very slowly, if at all, with potassium thiocyanate in absolute acetone; it has been shown by Straus⁷ that *tert.*-butyl chloride reacts like triphenylmethyl chloride, very readily with water in ethereal solution, but the latter reacts readily with calcium bromide and the former not at all.

Preparation of the Esters

Methyl Diphenylbromo-acetate.—Esters of diphenylchloro-acetic acid have long been known⁸ and the great reactivity of the chlorine atom in these compounds has frequently been recorded. Esters of the corresponding bromo acid have, however, hitherto been unknown. Unsuccessful attempts to prepare them in a state of purity are recorded by Salkind and Peschekerowa⁹ and by Klinger and Nickell.¹⁰

After a variety of methods had been tried without success, the following very simple procedure was found to give a good yield of methyl diphenylbromo-acetate. In a 100cc. Erlenmeyer flask connected with an air condenser by means of a ground-glass joint is placed 43.3 g. of phosphorus tribromide; 25.6 g. of bromine is then added through the top of the condenser during the course of 15 minutes. After the flask has cooled somewhat, 38.5 g. of methyl benzilate is added in portions, the flask being removed from the condenser for the addition of each portion. The ester is added at such a rate that the reaction does not at any time become violent. After all the ester has been added the flask is heated for 30 minutes on the steam-bath. The contents are then poured into a large mortar and triturated with ice and water, the water being frequently changed. After one-half to three-quarters of an hour the heavy, brown oil solidifies.

⁶ Conant, *THIS JOURNAL*, **47**, 488 (1925).

⁷ Straus, *Ann.*, **370**, 358, 364 (1909).

⁸ Jena, *Ann.*, **155**, 88 (1870). Bickel, *Ber.*, **22**, 1212, 1539 (1889). Klinger, *Ann.*, **389**, 253 (1912). Klinger and Standke, *Ber.*, **22**, 1211 (1889).

⁹ Salkind and Peschekerowa, *Chem. Zentr.*, **85**, II, 1269 (1914).

¹⁰ Klinger and Nickell, *Ann.*, **390**, 365 (1912).

The solid is thoroughly crushed, filtered and washed with water. After being dried it is recrystallized from a mixture of dry ether and petroleum ether, giving white crystals; m. p., 38.5–38.8°; yield, 37.5 g., or 77%.

Anal. Calcd. for $C_{12}H_{13}O_2Br$: Br, 26.20. Found: 26.15.

When impure, the ester decomposes quite rapidly, and even after it has been repeatedly crystallized it is rather unstable. A sample which had been carefully purified showed signs of beginning decomposition (appearance of brown spots) after standing stoppered in the laboratory for two months. It was then placed in a dark ice box. After three months it had completely liquefied and smelled of free bromine.

Action of Potassium Thiocyanate on Methyl Diphenylbromo-acetate

Preparation of Methyl Diphenylthiocyano-acetate.—Fourteen g. of methyl diphenylbromo-acetate and 9.1 g. of potassium thiocyanate in 100 cc. of absolute acetone were gently refluxed for five hours. A crystalline precipitate formed rapidly on warming and the solution became blue-green. The precipitate was filtered off and the excess of acetone was distilled from the filtrate. The residue on the addition of water gave 11 g. of solid. This was crystallized from dilute methyl alcohol and from a mixture of ether and ligroin, giving pure white crystals; m. p., 82.5–83.5°.

Anal. Calcd. for $C_{16}H_{15}O_2NS$: S, 11.33. Found: 11.38, 11.12.

Dimethyl Phenylbromomalonate.—The diethyl ester of phenylbromomalonate has been described by Wheeler and Johnson¹¹ as a colorless oil; b. p., 192° (20 mm.). My attempts to prepare this ester in a state of purity were unsuccessful. Diethyl phenylmalonate is readily brominated but the best fraction which could be isolated by repeated fractionation of the reaction product in a good vacuum was only 98% pure as indicated by the bromine content. Moreover, it could not be crystallized. Since a compound of high purity was desired, it was thought better to prepare the dimethyl ester.

To 41.6 g. of dimethylphenyl malonate dissolved in 50 cc. of chloroform in a small flask was added a crystal of iodine; 35.2 g. of bromine (10% excess) was then added in three or four portions through the top of the attached condenser with the aid of a dropping funnel. The reaction set in rapidly on gentle warming. After the addition of all of the bromine the mixture was boiled gently for two hours. The reaction mixture was then distilled. After the removal of the solvent, a red fore-fraction weighing 7.5 g. was collected. The main fraction, which was slightly yellow, then distilled at 170°–174° (8 mm.); yield, 45.7 g., or 80%. On being cooled and scratched it solidified. Recrystallized from a mixture of ether and petroleum ether it formed pure, white crystals; m. p., 45.5–46.5°.

Anal. Calcd. for $C_{11}H_{11}O_4Br$: Br, 27.84. Found: 27.86, 27.76.

¹¹ Ref. 4, p. 688.

Bromotricarbomethoxymethane.—Conrad¹² refers to the triethyl ester of chloromethane-tricarboxylic acid, and Johnson and Wheeler¹³ describe tricarbomethoxymethyl bromide as a colorless oil boiling for the most part at 162–163° (16 mm.). They found that it reacted with potassium thiocyanate with decomposition.

Tricarbomethoxymethane was prepared by the method of Scholl and Egerer.¹⁴ The yield and quality of the product were somewhat improved by stirring the mixture during the main reaction and by using a column in the distillation.

To 30 g. of tricarbomethoxymethane dissolved in 35 cc. of chloroform containing a crystal of iodine in a small flask provided with a reflux condenser, 26.7 g. of bromine in 20 cc. of chloroform was added in two portions. It was necessary to warm the flask to start the reaction. After boiling for two hours, the mixture (still containing some unchanged bromine) was distilled through a column. After the removal of the solvent a fore-fraction weighing 4.4 g. distilled, and then the main fraction, 37 g. Both fractions crystallized completely in the receiver. The substance was crystallized from a mixture of ether and petroleum ether. Slow crystallization gives beautiful, colorless, transparent, columnar crystals 5–6 mm. long; m. p., 50.5–51°; b. p., 116–117° (5 mm.).

Anal. Calcd. for $C_7H_9O_3Br$: Br, 29.70. Found: 30.02.

Summary

The reactivities of the compounds $(C_6H_5)_3CBr$ (I), $(C_6H_5)_2CBr(COOCH_3)$ (II), $(C_6H_5)CBr(COOCH_3)_2$ (III) and $CBr(COOCH_3)_3$ (IV) have been tested in a qualitative way toward the reagents silver nitrate in absolute acetonitrile, absolute methyl alcohol and potassium thiocyanate in absolute acetone. The results with the first two reagents indicate that the order of reactivity of these substances is $I > II > III > IV$ and with the last reagent $I > IV > II > III$.

The following compounds have been described: methyl diphenylbromoacetate, methyl diphenylthiocyanoacetate, dimethyl phenylbromomalonate, bromotricarbomethoxymethane.

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¹² Conrad, *Ber.*, **14**, 617 (1881).

¹³ Ref. 4, p. 687.

¹⁴ Scholl and Egerer, *Ann.*, **397**, 355 (1913).