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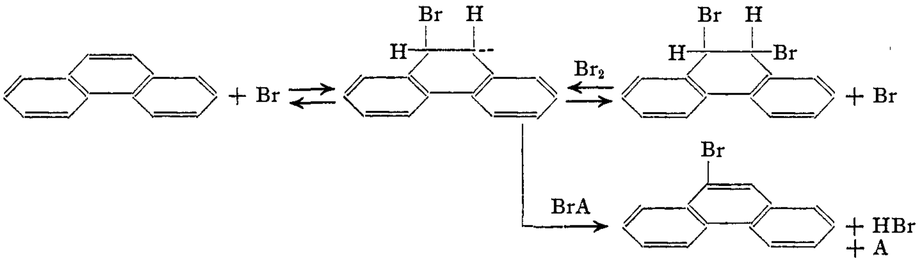
The Mechanism of Aromatic Bromination[1]

BY CHARLES C. PRICE AND CLYDE E. ARNTZEN

From previous investigations of the effect of iodine on the reaction between bromine and phenanthrene[2] it was concluded that the bromine substitution reaction proceeded in the following manner, A representing the necessary bromination catalyst.



Since the central ring of phenanthrene obviously differs from the usual aromatic type in that it forms a stable addition product, it remained to prove that this mechanism could be applied to aromatic compounds in general.

It was pointed out in a previous paper[2] that Bruner's[3] extensive measurements of the iodine-catalyzed bromination of benzene with this reactant as solvent could be reinterpreted very accurately according to the rate expression

$$d[C_6H_5Br]/dt = k[Br_2]^{3/2}[I_2]^{5/2}$$

Any dependence of the rate on the benzene concentration could not be detected in his experiments since the benzene was in such excess as to remain essentially unchanged during the course of the reaction.

A study of the iodine-catalyzed bromination of phenanthrene has shown it to obey the same kinetics as the similar reaction of benzene investigated by Bruner. The only difference is that it was not feasible to work with a large enough excess of phenanthrene for its concentration to remain unchanged during the course of the reaction. The rate expression therefore includes dependence on the hydrocarbon concentration as well as bromine and iodine.

$$d[C_{14}H_9Br]/dt = k[C_{14}H_{10}][Br_2]^{3/2}[I_2]^{5/2}$$

The values for the constant, k, calculated with the concentrations expressed in moles per liter, are summarized in Table I for various bromine, iodine and phenanthrene concentrations. The fact that for both benzene and phenanthrene the rate of bromination is dependent on the bromine concentration to the three-halves power and the iodine concentration to the five-halves power proves beyond reasonable doubt that the mechanisms for the two reactions are identical. We may therefore write the bromination of benzene according to the following scheme, omitting, of course, a dibromide such as is formed in the case of phenanthrene.

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(1) Presented before the Division of Organic Chemistry at the Dallas meeting of the American Chemical Society, April 19, 1938.

(2) Price, THIS JOURNAL, **58**, 2101 (1936).

(3) Bruner, *Z. physik. Chem.*, **41**, 514 (1902).

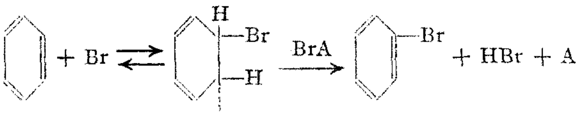


TABLE I

THE REACTION OF PHENANTHRENE AND BROMINE IN THE PRESENCE OF IODINE

$[I_2]$[a]	$[Br_2]$[a] = $[C_{14}H_{10}]$	k[b] × 10^{-5}	K_{25}[c]	K_{IBr}[d]
0.00204	0.0322	0.67		
.00204	.0644	.66	192	..
.00408	.0322	.64	133	..
.00408	.0644	.68		
.00613	.0322	.60	103	15
.00715	.0322	.60		
.00817	.0161	.59	94	16.5
.00817	.0322	.59	92	20
.00817	.0644	.65	96	19.5
.01022	.0322	.57	50	30
.01226	.0644	.54	37	24

[a] Total concentration expressed in moles per liter. [b] $d[C_{14}H_9Br]/dt = k[C_{14}H_{10}][Br_2]^{3/2}[I_2]^{5/2}$. [c] $K_{25} = [C_{14}H_{10}Br_2]/[C_{14}H_{10}][Br_2]$ (= 230 in absence of iodine). [d] $K_{IBr} = [IBr]/[Br_2]^{1/2}[I_2]^{1/2}$. K_{25}(Calcd.) = 19.9.

The catalyst may function in the reaction not only, as has been indicated, by the removal of hydrogen from the active intermediate, but also in the production of the active bromine which acts as the initiator of the reaction by producing this active intermediate. Thus the total effect of iodine on the rate of reaction may be divided into an effect on the equilibrium of the first step, the formation of the intermediate, in addition to catalysis of the second step, the removal of the hydrogen.

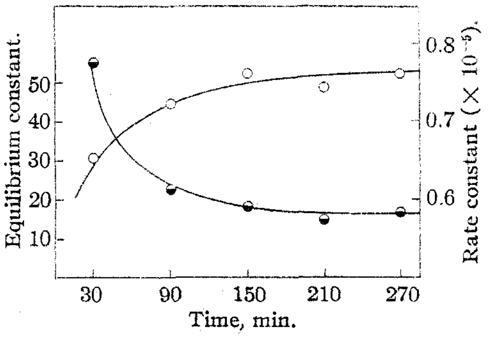
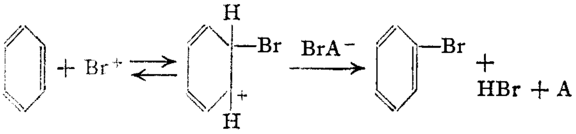


Fig. 1.—Phenanthrene and bromine concentration 0.0322 *M;* iodine 0.0102 *M;* equilibrium constant for addition ○; rate constant for substitution ●.

Since iodine has a decidedly inhibitory effect on the addition of bromine to phenanthrene,[2] which is a photochemical[4] chain reaction propagated by bromine atoms, it may well be that the iodine-catalysis of the first step in the bromination is the production of positive bromine *ions* rather than bromine atoms. The intermediate in this case would have a positive charge and would be that proposed by Pfeiffer and Wizinger.[5]



The fact that benzene reacts with bromine photochemically to form an addition product while the catalytic reaction leads to substitution is in agreement with this proposal. The photochemical addition most certainly proceeds by an atomic mechanism, leaving an ionic intermediate as the most probable for catalytic substitution in the absence of light.

The kinetics of the reaction are incapable of distinguishing between the atomic and the ionic mechanisms, proving only that the same mechanism holds for both benzene and phenanthrene.

The experiments were all performed in the dark using painted flasks to exclude light. Bromine was purified as in previous experiments;[6] the iodine was resublimed and the phenanthrene prepared from its recrystallized dibromide by treatment with zinc dust in alcohol,[4b] m. p. 99–99.5°.

Standard solutions of the three reagents were mixed and the samples for individual titrations immediately placed in small (5-cc.) glass-stoppered flasks and sealed with paraffin to prevent loss of hydrogen bromide. After a specified interval the flasks were opened under distilled water containing potassium iodide. The liberated iodine was titrated with sodium thiosulfate to the disappearance of its color, then the acid with carbonate-free sodium hydroxide using phenolphthalein as indicator. From these data the course of both addition and substitution can be determined since the decrease in bromine concentration is a measure of both reactions while the acid is produced by substitution alone.

It was found in every case that the rate constant for the substitution reaction did not become truly constant until the equilibrium of the addition reaction had been established. In Fig. 1 are plotted the rate and equilibrium constants at various times for a typical experiment to illustrate this point. The rate constants of Table I are, therefore, the average of the individual con-

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(4) (a) Kharasch, White and Mayo, *J. Org. Chem.*, **2**, 574 (1938); (b) Price, Arntzen and Weaver, THIS JOURNAL, **60**, 2837 (1938).

(5) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

(6) Price, THIS JOURNAL, **58**, 1834 (1936).

stants for each experiment after the attainment of the equilibrium of the addition reaction.

In Table I the penultimate column lists the values for the equilibrium constants for the addition of bromine to phenanthrene at the various iodine concentrations. They show a steady decrease with increasing iodine concentration which may be accounted for by the reaction of bromine and iodine to form a bromoiodide

$$Br_2 + I_2 \rightleftarrows BrI$$

which would reduce the actual concentration of bromine molecules but not the bromine titer. Insertion of the titer value for bromine, a larger value than is actually effective, would cause a variation in the manner noted for the equilibrium constant.

In fact, since the true value for the equilibrium constant, $K_{25} = [C_{14}H_{10}Br]/[C_{14}H_{10}][Br_2] = 230$, is known, and since the concentrations of both the phenanthrene and its dibromide may be calculated from the experimental data, it is possible to calculate from this the value for the free molecular bromine concentration. With this value known, as well as the total iodine and total bromine concentrations (Br_2 + BrI) it is possible to calculate the equilibrium constant, $K_{IBr} = [BrI]/[Br_2]^{1/2}[I_2]^{1/2}$, for the bromine–iodide reaction in carbon tetrachloride solution, the values for which are given in the final column of Table I. The calculation is for the last determination in each experiment, which should be at equilibrium. No calculation could be made for the experiments at lower iodine concentration since the equilibrium of the addition reaction had not been established at the last measurement.

Bodenstein and Schmidt[7] have determined the value for this equilibrium constant at elevated temperatures in the gas phase and derived the following expression for its dependence on the temperature

$$\log \frac{1}{4K^2} = \frac{3.676}{4.57 \times T} - 0.50$$

Calculation of the equilibrium constant at 25° from this expression gives a value of 19.9, agreeing well with the experimentally determined values, especially since a fairly large experimental error (10–15%) could easily be involved.

Summary

The kinetics of the iodine-catalyzed bromination of phenanthrene have been determined as identical with those of benzene. This is offered as proof of the identity of mechanism for the bromination of aromatic compounds in general with that previously proposed for phenanthrene.

This mechanism involves addition of a positive bromine ion to the unsaturation of the aromatic nucleus followed by catalytic elimination of a hydrogen ion to yield the substitution product.

It has been found that the equilibrium for the bromine-iodine reaction in carbon tetrachloride solution agrees with the determinations of Bodenstein and Schmidt for the gas phase reaction at considerably higher temperatures.

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(7) Bodenstein and Schmidt, *Z. physik. Chem.*, **123**, 30 (1926).

URBANA, ILLINOIS RECEIVED JULY 1, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction of Bromine with Various Samples of Phenanthrene

BY CHARLES C. PRICE, CLYDE E. ARNTZEN AND CLAY WEAVER

No entirely satisfactory method for the purification of phenanthrene has as yet been developed. Selective oxidation with nitric acid[1] and with chromic acid,[2] as well as treatment with maleic anhydride,[3] have been recommended for the removal of anthracene. Treatment with sodium has been found effective for the removal of fluorene[4] or sulfur-containing compounds.[5]

We have found the following series of reactions convenient for preparing samples of phenanthrene of a high degree of purity from relatively impure starting material.

$$C_{14}H_{10} + Br_2 \longrightarrow C_{14}H_{10}Br_2 \xrightarrow[\substack{\text{alcohol}\\(60°)}]{\text{Zn dust in}} C_{14}H_{10} + ZnBr_2$$

The chief advantage offered is that the phenanthrene dibromide may be recrystallized to remove impurities which could not be separated from phenanthrene itself by crystallization. The prod-

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(1) Cohen and Cormier, THIS JOURNAL, **52**, 4363 (1930).

(2) W. E. Bachmann, *ibid.*, **57**, 557 (1935).

(3) Clar, *Ber.*, **65**, 852 (1932).

(4) Jeanes and Adams, THIS JOURNAL, **59**, 2615 (1937).

(5) Schroeter, *Ber.*, **57**, 2025 (1924).