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.

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

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[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.

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

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).

uct so obtained (A) melted at 99–99.5°, three degrees higher than the starting material, which had been purified by oxidation[2] but not by treatment with sodium.

Dihydrophenanthrene was a possible impurity in this product since some of the dibromide might decompose with evolution of hydrogen bromide even though the temperature was kept well below its usual thermal decomposition point (90–100°). Consequently some of the material (A) was treated with selenium for eight hours at 300–320°, distilled and twice recrystallized. This treatment raised the melting point only half a degree but completely altered the behavior of the material toward bromine.

Phenanthrene purified from coal tar as described previously[6] and the sample (A) prepared by the present method react with bromine photochemically[7] at nearly the same rapid rate. The sample from selenium treatment, however, in spite of the higher melting point, was found to react only very slowly, although it finally attained the same equilibrium for the addition reaction as the other samples. This is in agreement with experiments using synthetic phenanthrene,[8] which also had been treated with selenium. This material was found to melt high (m. p. 100.7–101°), and to react with bromine only very slowly.

That the difference in the behavior of these various samples of phenanthrene was not due to the absence of fluorene or anthracene in the selenium-treated samples (which may have been present as an impurity in the material reacting with bromine), was demonstrated by addition of these hydrocarbons to such samples, the mixtures showing the same characteristics as the original material.

It was of interest to note that anthracene, which catalyzes several reactions of bromine in the dark,[9] did not cause the chain addition of bromine to phenanthrene. The course of the reaction of bromine with a mixture of phenanthrene and anthracene appeared, in this case, to be the addition of one molecule of bromine to phenanthrene for each molecule reacting with anthracene. The results of these experiments are summarized in Table I. The fact that all the phenanthrene samples behave similarly in this instance indicates that the material which inhibits the photochemical addition (bromine atom mechanism) has no effect on the dark, anthracene-catalyzed reaction (bromine cation mechanism).

TABLE I

THE DARK REACTION OF PHENANTHRENE AND ITS DIBROMIDE WITH BROMINE IN THE PRESENCE OF ANTHRACENE

[Phenanthrene] = [Br_2] = 0.03 *M;* time, 60 minutes.

[Anthracene]	Δ[Br_2]	Δ[Br_2] for anthracene	Δ[Br_2] for phenanthrene
....	0.0005	....	0.0005
0.0005[a]	.0025	0.0010	.0015
.00065[b]	.0030	.0013	.0017
.00075[c]	.0033	.0015	.0018
[Phenanthrene Dibromide] = 0.03 *M;* [Br_2] = 0.003 *M;* time, 30 minutes			
....	−0.0003	....	−0.0003
0.00065	− .0001	0.0013	− .0014

[a] Phenanthrene sample (A). [b] Phenanthrene sample (A) treated with selenium. [c] Gesellschaft für Teerverwertung phenanthrene.

Furthermore, it was found that addition of selenium-treated phenanthrene to that reacting with bromine gave a mixture which would not react. These various facts are interpreted as indicative of the presence of an inhibitor in the phenanthrene treated with selenium, in spite of its higher melting point. However, since the photobromination of this hydrocarbon is a chain reaction of considerable length,[6] it would require but small amounts of a chain-breaking impurity to account for the results.

Several qualitative tests have been made for the purity of the various samples of phenanthrene. These are summarized in Table II.

These color tests indicate that the samples prepared by the present method are much purer than the starting material and seem quite similar to a sample of the highly purified hydrocarbon from the Gesellschaft für Teerverwertung.

Experimental

Crude phenanthrene (10 g.) with a melting point of 94–96° was dissolved by warming in 50 cc. of purified[6] carbon tetrachloride[10] and, after cooling in ice, treated with 4 cc. of bromine in portions. The reaction mixture was allowed to stand in sunlight at 0° for an hour. The dibromide, 13 g. (65%), was recrystallized by dissolving in the minimum amount of benzene (150 cc.) at 40–45°,[11] adding an equal amount of petroleum ether (60–90°), and cooling in an ice-salt bath to −15°. The pure dibromide, crystallizing as colorless plates with a greenish tinge, was collected by filtration, yield 10 g., m. p. 98–99°, with decomposition. Its

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

[7] All rates mentioned are for the photochemical reaction unless specified otherwise.

[8] Fieser and Hershberg, THIS JOURNAL, **57**, 2192 (1935).

[9] (a) Price and Thorpe, *ibid.*, **60**, 2839 (1938); (b) Price and Weaver, unpublished work.

[10] The reaction of bromine with phenanthrene in commercial carbon tetrachloride was found to proceed much more slowly and a much poorer yield of the dibromide was obtained.

[11] Since anthracene dibromide is very unstable even at room temperature, it should be decomposed completely by this treatment.

TABLE II

COLOR TESTS ON VARIOUS HYDROCARBON SAMPLES

Compound	H_2SO_4 Cold	H_2SO_4 Warm	H_2SO_4-HNO_3[a]	H_2SO_4-40% Formalin[a]
Phenanthrene				
(1) Crude	Yellow	Dark yellow	Red-black	Blue crystals (tan soln.)
(2) Sample (A) (3) (A) treated with Se (4) Commercial[b]	None	Very pale blue	Clear red	Blue crystals (colorless soln.)
Anthracene[c]	Yellow	Black		Dark brown-black soln.
Fluorene[b]	None	None	Pale yellow	Deep purple soln. (5 min.)

[a] The hydrocarbon was suspended in sulfuric acid and one drop of the second reagent was added.

[b] Gesellschaft für Teerverwertung.

[c] Martin, THIS JOURNAL, **58**, 1438 (1936).

solution in 200 cc. of alcohol was treated with 7.5 g. of zinc dust at 50–60° for twelve hours, the reaction mixture filtered while hot, evaporated to 50–60 cc. and set aside to crystallize. The yield was 4.6 g. (90%) of colorless plates melting at 99–99.5° after one recrystallization.

A portion of this material was heated with selenium to 300–320° for eight hours, distilled under diminished pressure and twice recrystallized from alcohol to give a sample melting at 99.5–100°.

Summary

Phenanthrene of a high degree of purity may be obtained by conversion to the dibromide followed by regeneration of the hydrocarbon on treatment with zinc dust.

Phenanthrene which has been treated with selenium apparently contains an impurity inhibiting the photochemical addition of bromine.

Anthracene has been found to catalyze an equimolecular but not a chain addition of bromine to phenanthrene in the dark.

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A Chemically-Catalyzed cis-trans Isomerization

BY CHARLES C. PRICE AND RALPH S. THORPE

The anthracene-catalyzed bromination of dioxane[1] can be accounted for only by assuming that the reaction between bromine and anthracene produces active bromine. Since many photochemical reactions of bromine presumably proceed through active bromine atoms produced by the dissociation of a bromine molecule on absorption of light, and since the same intermediate has been proposed for several reactions of hydrogen bromide in the presence of peroxides,[2] it was proposed to use one of these reactions to test the possibility that the active bromine produced by the anthracene–bromine reaction in the dark might behave in a similar manner.

The particular reaction studied was the conversion of a maleic ester to the corresponding fumaric ester. Wachholtz and Schmidt[3] have reported previously the photochemical isomerization of the ethyl and methyl esters, respectively, in the presence of bromine. Both investigators agree that the mechanism must be a chain reaction with a length of several hundred, initiated by the photochemical dissociation of bromine molecules to atoms. They represent the course of the reaction as

$$Br_2 + h\nu \longrightarrow 2Br$$

$$M + Br \longrightarrow (MBr) \longrightarrow F + Br$$

More recently Kharasch[2] has proposed a bromine atom intermediate for the peroxide-catalyzed rearrangement of isostilbene to stilbene in the presence of hydrogen bromide, and, on this basis, has extended this proposal of a bromine atom mechanism to the well-known effect of peroxides in reversing the usual mode of addition of hydrogen bromide to many olefinic double bonds.

The investigation reported herein is on the conversion of ethyl maleate to ethyl fumarate by bromine and anthracene in carbon tetrachloride solution.

Experimental.—The reactions were all carried out in purified carbon tetrachloride solution.

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[1] Price and Weaver, unpublished work.

[2] Kharasch, Mansfield and Mayo, THIS JOURNAL, **59**, 1155 (1937).

[3] (a) Wachholtz, *Z. physik. Chem.*, **125**, 1 (1929); (b) Schmidt, *bid.*, **B1**, 205 (1930).