Phenanthrene–Silver Ion Complexes in Trifluoroacetic Acid, and their Influence on the Rates of Detritiation of [9-^{3}H]Phenanthrene in the Presence of Silver Trifluoroacetate

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Silver trifluoroacetate has a marked inhibiting effect on detritiation of [9-^{3}H]phenanthrene, P, in trifluoroacetic acid at 100°. A rough analysis of the rates of detritiation at various concentrations of hydrocarbon and silver salt in the light of equilibrium constants for the several complexes deduced from spectroscopic studies at 20° indicates that the $[P{\cdot}Ag]^+$ complex is only a few times less reactive than free phenanthrene, and is more reactive than the $[2P{\cdot}Ag]^+$ complex.

Detritiation of [1-^{3}H]phenanthrene is retarded by silver trifluoroacetate by about the same factor as that for [9-^{3}H]phenanthrene. Silver trifluoroacetate inhibition of detritiation decreases in the sequence [9-^{3}H]phenanthrene > [1-^{3}H]naphthalene > [2-^{3}H]-*p*-xylene, in line with the decreasing strength of the complexes with silver ion.

The electronic spectrum of phenanthrene in the presence of silver trifluoroacetate has been analysed on the assumption that 1 : 1, 1 : 2, and 2 : 1 complexes are formed between phenanthrene and silver ion. The degree of complex formation is much greater than that in aqueous solutions at corresponding concentrations, and the following equilibrium constants (at 20 °C) have been derived: $K_{11} = 5{\cdot}1 \times 10^4$ l mol^{-1}, $K_{12} = 1{\cdot}4 \times 10^7$ l^2 mol^{-2}, and $K_{21} = 3{\cdot}3 \times 10^6$ l^2 mol^{-2}. For the 1 : 1 complex there is a small shift of the first phenanthrene absorption band to lower frequencies and a small increase in intensity. The first absorption band of the 2 : 1 complex has much greater intensity, suggesting that there is an exciton interaction between the two phenanthrene molecules.

WE describe below the results of some kinetic and spectroscopic studies of the interaction between phenanthrene and silver trifluoroacetate in trifluoroacetic acid.

Kinetic Studies.—As part of a series of investigations of detritiation of tritiated aromatic compounds in anhydrous trifluoroacetic acid,[1] the effects of some trifluoroacetate salts on the rate of detritiation of [9-^{3}H]-phenanthrene were examined. It was found that whereas with $5{\cdot}62 \times 10^{-3}$M-[9-^{3}H]phenanthrene, 0·1M-sodium trifluoroacetate or lithium trifluoroacetate caused a small increase in rate, the same concentration of silver trifluoroacetate caused a 30-fold decrease in rate (Table 1). In view of the results with lithium and sodium salts, this large influence of silver trifluoroacetate was clearly not attributable to a general kinetic salt effect, and we suspected that it was associated with the formation of a complex or complexes between the phenanthrene and the silver ion. Such species are known to form in aqueous solution and the positively-charged complexes would be expected to be less reactive than phenanthrene towards the electrophilic reagent. It was clear, however, that the equilibrium constants for formation of the complexes in trifluoroacetic acid would have to be substantially larger than those in water to account for the rate effects. For example, in an aqueous solution of $5{\cdot}6 \times 10^{-3}$M-phenanthrene and 0·20M-silver ion at 25 °C only about half the phenanthrene would be complexed,[2] whereas at these concentrations in trifluoroacetic acid at 100° the rate of detritiation was found to be 70 times smaller than that in the absence of silver salt.

TABLE 1

Effects of trifluoroacetates on the rates of detritiation of tritiated aromatic hydrocarbons ($5{\cdot}62 \times 10^{-3}$M) in trifluoroacetic acid

Hydrocarbon	Salt	[Salt]/M	T/°C	10^7k/s^{-1}	k/k_0
[9-^{3}H]Phenanthrene	None		100	1605	1·00
	None		70	156	1·00
	None		50	23·3	1·00
	$LiO_2C{\cdot}CF_3$	0·010	100	1765	1·10
	$NaO_2C{\cdot}CF_3$	0·010	100	1700	1·06
	$AgO_2C{\cdot}CF_3$	0·010	100	605	0·38
		0·010	70	48·7	0·31
		0·010	50	5·57	0·24
[1-^{3}H]Phenanthrene	None		100	924	1·00
	$AgO_2C{\cdot}CF_3$	0·010	100	380	0·41
[1-^{3}H]Naphthalene	None		100	159 [a]	1·00
	$AgO_2C{\cdot}CF_3$	0·050	100	123	0·12
[2-^{3}H]-*p*-Xylene	None		100	1200	1·00
	$AgO_2C{\cdot}CF_3$	0·050	100	180	0·15
[2-^{3}H]-*p*-Xylene [b]	$AgO_2C{\cdot}CF_3$	0·050	100	432	0·36

[a] Value at 100·7° reported by C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1112. [b] In presence of $5{\cdot}06 \times 10^{-2}$M-phenanthrene.

In an attempt to throw light on the nature of the complexes involved, rates of detritiation were measured

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[1] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97 and earlier papers in the same series.

[2] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1949, **71**, 3644.

for a range of concentrations of phenanthrene and silver trifluoroacetate at 100 °C, as shown in Table 2, in which k is the observed first-order rate constant and k/k_0 the rate relative to that in absence of salt. An initial attempt was made to interpret the rate variations by assuming that only a 1 : 1 complex, $[P{\cdot}Ag]^+$, was formed, and that only the free phenanthrene reacted; this was not successful, and the analysis indicated that other complexes probably including a 2 : 1 complex, $[2P{\cdot}Ag]^+$, were also formed. Spectroscopic data for a variety of aromatic compounds in aqueous solution have previously been interpreted in terms of $[Ar{\cdot}Ag]^+$ and $[Ar{\cdot}2Ag]^{2+}$ complexes.[2,3]

TABLE 2

Effects of silver trifluoroacetate on the rate of detritiation of [9-^{3}H]phenanthrene in trifluoroacetic acid at 100·0°

Run no.	$10^3 \times$ [Phenanthrene]/M	$10^3 \times [AgO_2C{\cdot}CF_3]$/M	10^7k/s^{-1}	k/k_0	(k/k_0) calc.
1	5·62	0·00	1605	1·00	1·00
2		2·50	1137	0·71	0·70
3		5·00	932	0·58	0·56
4		10·0	605	0·38	0·36
5		20·0	338	0·21	0·18
6		50·0	171	0·073	0·090
7		100	54	0·036	0·060
8		200	24·5	0·015	0·056
9	33·7	10	1025	0·64	0·62
10	22·5	10	844	0·53	0·55
11	11·25	10	690	0·43	0·53
12	2·81	10	567	0·35	0·25

Spectroscopic studies of the complexes were then carried out on more dilute solutions at room temperature (*ca.* 20 °C) as described below, and indicated that 1 : 1, 2 : 1, and 1 : 2 complexes are all formed. The corresponding equilibrium constants K_{11}, K_{21}, and K_{12} were derived, and use of these constants enabled calculation of the concentration, P, C_{11}, C_{21}, C_{12}, of the free phenanthrene and the complexes $[P{\cdot}Ag]$, $[2P{\cdot}Ag]^+$, and $[P{\cdot}2Ag]^{2+}$, respectively, which would exist at room temperature in the solutions used for the rate studies, and these are shown in Table 3. Unfortunately the spectroscopic studies could not be carried out at a temperature at which the exchange rates could be conveniently measured, and in order to carry forward the analysis we first make the extreme simplifying assumption that the concentrations of the complexes at 100° are not greatly different from those at 20°, and later consider the magnitude of the uncertainty introduced by this assumption. Using the concentrations as defined above, the rate of detritiation during any one run should be given by equation (1), in which

$$kP_0 = k_0P + k_{11}C_{11} + k_{21}C_{21} + k_{12}C_{12} \qquad (1)$$

k_0, k_{11}, k_{21}, and k_{12} are the respective rate constants for detritiation of phenanthrene and the 1 : 1, 2 : 1, and 1 : 2 complexes. Expression of the values of the rate constants relative to k_0, and of concentrations relative to the total phenanthrene concentration, P_0, taken in each case, leads to equation (2). When the observed

$$\frac{k}{k_0} - \frac{P}{P_0} = \frac{k_{11}C_{11}}{k_0\,P_0} + \frac{k_{21}C_{21}}{k_0P_0} + \frac{k_{12}C_{12}}{k_0P_0} \qquad (2)$$

values of k/k_0 and the derived concentrations of each species were inserted into this equation, a least-squares analysis gave the best values of k_{11}/k_0, k_{21}/k_0, and k_{12}/k_0 as 0·57, 0·050, and 0·00 respectively, with the values of k_{21}/k_0 and k_{12}/k_0 subject to much greater uncertainty than those of k_{11}/k_0. The fit between observed and calculated values of k/k_0 (see Table 2) must be regarded as satisfactory in view of the approximations involved; the only serious deviations refer to conditions in which a great excess of silver trifluoroacetate is present, which might introduce salt effects not allowed for in the calculations. A better fit could clearly be obtained under these conditions by assigning a small finite value to k_{12}/k_0 in place of the zero value which leads to the best fit over all the data.

TABLE 3

Calculated concentrations at 20° of free hydrocarbon, P, and the several complexes, C_{xy}, in the trifluoroacetic acid solutions of phenanthrene and silver trifluoroacetate used in detritiation studies.

Run no.[a]	P	C_{11}	C_{12}	C_{21}
2	$2{\cdot}8 \times 10^{-3}$	$2{\cdot}1 \times 10^{-3}$	$8{\cdot}8 \times 10^{-6}$	$3{\cdot}8 \times 10^{-4}$
3	$7{\cdot}0 \times 10^{-4}$	$4{\cdot}4 \times 10^{-3}$	$1{\cdot}5 \times 10^{-4}$	$2{\cdot}0 \times 10^{-4}$
4	$3{\cdot}0 \times 10^{-5}$	$3{\cdot}4 \times 10^{-3}$	$2{\cdot}2 \times 10^{-3}$	$6{\cdot}8 \times 10^{-6}$
5	$2{\cdot}8 \times 10^{-6}$	$1{\cdot}5 \times 10^{-3}$	$4{\cdot}2 \times 10^{-3}$	$2{\cdot}7 \times 10^{-7}$
6	$2{\cdot}4 \times 10^{-6}$	$4{\cdot}7 \times 10^{-4}$	$5{\cdot}1 \times 10^{-3}$	$7{\cdot}4 \times 10^{-9}$
7	$4{\cdot}9 \times 10^{-8}$	$2{\cdot}2 \times 10^{-4}$	$5{\cdot}4 \times 10^{-3}$	$7{\cdot}0 \times 10^{-10}$
8	$1{\cdot}1 \times 10^{-8}$	$1{\cdot}1 \times 10^{-3}$	$5{\cdot}5 \times 10^{-3}$	$7{\cdot}6 \times 10^{-11}$
9	$1{\cdot}83 \times 10^{-2}$	$4{\cdot}5 \times 10^{-3}$	$6{\cdot}2 \times 10^{-6}$	$5{\cdot}5 \times 10^{-3}$
10	$8{\cdot}9 \times 10^{-3}$	$6{\cdot}3 \times 10^{-3}$	$2{\cdot}5 \times 10^{-5}$	$3{\cdot}7 \times 10^{-3}$
11	$1{\cdot}1 \times 10^{-3}$	$8{\cdot}5 \times 10^{-3}$	$3{\cdot}6 \times 10^{-4}$	$6{\cdot}3 \times 10^{-4}$
12	$4{\cdot}0 \times 10^{-6}$	$1{\cdot}1 \times 10^{-3}$	$1{\cdot}7 \times 10^{-3}$	$2{\cdot}9 \times 10^{-7}$

[a] See Table 2.

The only features worthy of further discussion are (i), the apparent reactivity of the $[P{\cdot}Ag]^+$ complex is much greater than might have been expected for a charged species, and (ii) the apparent reactivity of this complex is not only markedly greater than that of the $[P{\cdot}2Ag]^{2+}$ complex, as expected in view of the large positive charge on the latter, but is also substantially greater than that of the $[2P{\cdot}Ag]^+$ species, even though in the latter any charge transferred from the silver ion is shared between two molecules of phenanthrene. To

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[3] J. N. Murrell and S. Carter, *J. Chem. Soc.*, 1964, 6185.

decide whether these features are real it is necessary to consider the probable effects of the difference in temperature between the spectroscopic and the rate studies.

Results in Table 1 show that the value of k/k_0 at the fixed concentrations of phenanthrene and silver salt concerned falls from 0·38 to 0·24 on going from 100 to 50°. It probably falls by roughly a similar factor on going from 50 to 20°, so that the value of k/k_0 would probably be *ca.* 3 times smaller at 20 than at 100°. The concentrations of the several species present will not all change by the same amount on varying the temperature, but, even so, in view of the comparative smallness of the effect of temperature on k/k_0 it seems safe to conclude that the $[\mathrm{P{\cdot}Ag}]^+$ complex is only a few times less reactive than free phenanthrene and, furthermore, that it is more reactive than the $[\mathrm{2P{\cdot}Ag}]^+$ complex. The unexpectedly high reactivity of the 1 : 1 complex may perhaps be attributable to the fact that the effective charge on the silver ion is reduced by solvation of one side of the ion, and possibly also by ion pairing with trifluoroacetate ion. With the $[\mathrm{2P{\cdot}Ag}]^+$ complex, on the other hand, in which the silver ion lies between the two phenanthrene molecules, direct interaction of the solvent with the silver centre would be completely inhibited, and in view of the dispersion of the positive charge over a large system both general solvation and ion-pairing would be ineffective. Thus a markedly greater proportion of charge might be transferred to each aromatic molecule in the 2 : 1 complex than is transferred to the one molecule in the 1 : 1 complex. It is also conceivable that the silver ion is associated with the outer rings of the phenanthrene in the 1 : 1 complex but with the central ring, and perhaps even specifically with the 9,10 C⁚C bond, in the 2 : 1 complex, though if the silver ion were associated specifically with one bond in the 1 : 1 complex this could be expected to be the 9,10 bond, which has the greatest π-electron density. In the hope of throwing some light on this question of interaction of the silver ion with a particular bond, the effects of silver trifluoroacetate (0·01M) on the rates of reaction of [1-^{3}H]- and [9-^{3}H]-phenanthrene (5·62 × 10^{-3}M) at 100° were compared. The rate was reduced 2·4 times for the former and 2·6 times for the latter, indicating little selectivity in the effect of the silver ion.

A brief study was made of the comparative effects of silver trifluoroacetate on the rates of detritiation of [2-^{3}H]-*p*-xylene, [1-^{3}H]naphthalene, and [9-^{3}H]phenanthrene. With a 5·62 × 10^{-3}M-concentration of the aromatic compound, addition of 0·050M-silver trifluoroacetate reduced the rates for tritiated xylene, naphthalene, and phenanthrene by factors of 6·6, 8·5, and 13·7, respectively, a sequence consistent with the increasing stability of the hydrocarbon–silver ion complexes in water,[2] and presumably in trifluoroacetic acid also. Consistently the rate of detritiation of [2-^{3}H]-*p*-xylene (0·0056M) in presence of silver trifluoroacetate (0·050M) was increased 2·4 times when an excess of inactive phenanthrene (0·051M) was added, showing that the silver ion is preferentially taken up by the phenanthrene.

Spectroscopic Studies.—Spectroscopically the silver ion–hydrocarbon complexes are of interest as they are relatively simple examples of the important class of donor–acceptor complexes. They are, however, difficult to study spectroscopically because their absorption bands are overlayed by the bands of the free hydrocarbon. Thus the charge-transfer band of the $\mathrm{Ag^+}$–benzene complex lies at shorter wavelengths than the first benzene (260 nm) band.[3] Although the complex formation between silver ion and phenanthrene which we have studied is so strong that conditions can be established under which little free hydrocarbon remains, the analysis is complicated by the fact that more than one complex is certainly present under these conditions.

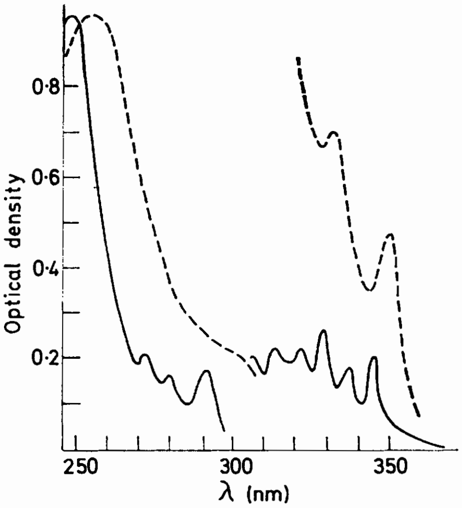

FIGURE 1 A plot against the wavelength, λ, of the optical densities of 1·91 × 10^{-4}M-solutions of phenanthrene in (a) (solid line) trifluoroacetic acid, (b) (broken lines) trifluoroacetic acid containing 0·10M-silver trifluoroacetate. A cell path length of 1·0 cm was used below 310 nm and one of 5·0 cm above 310 nm

Figure 1 shows the spectrum of 1·91 × 10^{-4}M-phenanthrene in trifluoroacetic acid alone and in the presence of 0·1M-silver trifluoroacetate. We shall show later that the solution with silver salt contains less than 0·001% of free phenanthrene.

In the long wavelength region, the weak phenanthrene ^1L_b band, which shows six pronounced vibrational components, is replaced by a stronger band with just two peaks. This absorption commences at slighly longer wavelengths than the free phenanthrene band. The ^1L_a band of phenanthrene at 290 nm is replaced by a broad shoulder at 300 nm of similar intensity, and the intense B_b band at 250 nm is slightly shifted to lower energies. For quantitative study the most convenient wavelength is 350 nm because at this value the uncomplexed molecule absorbs relatively weakly. The second absorption maximum of the complexes is at 333 nm and is also reasonably satisfactory, as this coincides with a minimum in the uncomplexed phenanthrene spectrum. We have also examined the absorption at 300 nm, this being a shoulder in the spectrum of the complex.

Three series of solutions were studied: (*a*) equimolar solutions of phenanthrene (P) and silver salt (A), with concentrations ranging from 2 to 60×10^{-4}M; (*b*) with constant silver salt (2×10^{-4}M) and concentrations of phenanthrene up to 60×10^{-4}M; and (*c*) with constant phenanthrene (5×10^{-4}M) and silver salt concentrations up to 60×10^{-4}M. The optical density at 350 nm was recorded for each of these solutions in a 1 cm cell balanced against trifluoroacetic acid. Solutions of silver trifluoroacetic acid in trifluoroacetic acid show a negligible absorption at this wavelength.

The data were interpreted on the assumption that 1 : 1, 1 : 2, and 2 : 1 complexes were present. For selected values of the three equilibrium constants, K_{11}, K_{12}, and K_{21}, extinction coefficients were found which gave the best fit to the observed optical densities D, according to equation (3). The concentrations of the

$$D = P\varepsilon_p + C_{11}\varepsilon_{11} + C_{12}\varepsilon_{12} + C_{21}\varepsilon_{21} \qquad (3)$$

complexes are determined by the values of the equilibrium constants and the constraint equations (4) and (5),

$$P_0 = P + C_{11} + C_{12} + 2C_{21} \qquad (4)$$

$$A_0 = A + C_{11} + 2C_{12} + C_{21} \qquad (5)$$

in which P_0 and A_0 are the measured total amounts (free and complexed) of phenanthrene and silver salt respectively. Equations (4) and (5) may be solved iteratively for P and A if the concentrations of the complexes are replaced by using equation (3). A computer programme was written which gave the best values of the six parameters K_{11}, K_{12}, K_{21}, ε_{11}, ε_{12}, and ε_{21} according to a least-squares fit to 41 measurements of D in the ranges described. The following results were obtained:

$K_{11} = 5{\cdot}1 \times 10^4$ l mol^{-1} $\qquad \varepsilon_{11} = 200$

$K_{12} = 1{\cdot}4 \times 10^7$ l^2 mol^{-2} $\qquad \varepsilon_{12} = 510$

$K_{21} = 3{\cdot}3 \times 10^6$ l^2 mol^{-2} $\qquad \varepsilon_{21} = 3800$

The data were thus fitted by a six-dimensional function, and, not surprisingly, the resulting surface was very shallow in some dimensions. The products $K\varepsilon$ are quite accurately determined by the data, but there is a large uncertainty in the individual values of K and ε. The standard deviation, Σ, between the observed and calculated optical densities appropriate to the best set of parameters is $1{\cdot}8 \times 10^{-4}$ which implies an average deviation between the observed and calculated values of D of *ca.* 0·01 absorbance units, which is close to the experimental limit of the spectrometer. As a measure of the accuracy we record the increase in the standard deviation on changing the equilibrium constants independently; if R_i, which measures the rate of increase of Σ as K_i as changed from its optimum value,

$$R_i = K_i^2 \frac{d^2\Sigma}{dK_i^2} \approx \frac{2K_i^2(\Sigma - \Sigma_0)}{\Delta K_i^2} \qquad (6)$$

is defined as in expression (6), then the values appropriate to the several equilibrium constants are as follows:

	K_{11}	K_{12}	K_{21}
R_i	$4{\cdot}0 \times 10^{-4}$	$4{\cdot}7 \times 10^{-5}$	$3{\cdot}2 \times 10^{-4}$

It is apparent that K_{12} can be obtained with less precision than K_{11} and K_{21}.

From these values of the equilibrium constants we can determine the concentrations of the three complexes and of free phenanthrene and silver ion. Figure 2 shows the results for the three series of measurements (a, b, and c) defined above. For the solution whose spectrum is shown in Figure 1 we deduce the following concentrations:

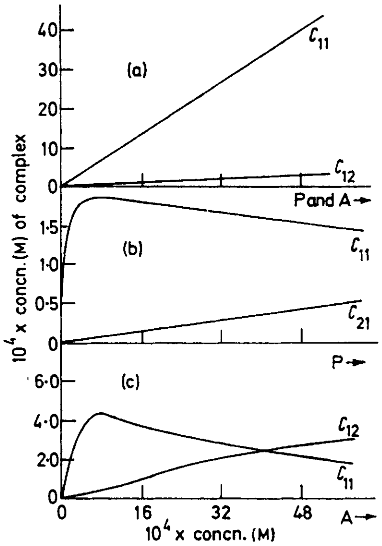

FIGURE 2 Plots of the concentrations of the several complexes against (a) the (equimolar) concentrations of phenanthrene and silver trifluoroacetate, (b) the concentration of phenanthrene at a fixed silver trifluoroacetate concentration of $2{\cdot}0 \times 10^{-4}$M, and (c) the concentration of silver trifluoroacetate at a fixed phenanthrene concentration of 5×10^{-4}M

P, $1{\cdot}33 \times 10^{-9}$M; C_{11}, $6{\cdot}61 \times 10^{-6}$M;
C_{12}, $1{\cdot}84 \times 10^{-4}$M; C_{21}, $5{\cdot}81 \times 10^{-13}$M

The first prominent band in Figure 1, which is the one used for the above analysis, appears only at high concentrations of silver salt. We can, therefore, be reasonably certain that it is not due to the $[2P{\cdot}Ag]^+$ complex although this species has been found to have the largest extinction coefficient in this region. When two phenanthrene molecules are associated in the same complex we would expect a long range exciton-type interaction between the states which give rise to the intense bands in the phenanthrene spectrum (^1L_a and B_b).[4] The interaction would shift one component of these bands to lower energies. This would explain the larger extinction coefficient of the $[2P{\cdot}Ag]^+$ complex in the 350 nm region.

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[4] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963, ch. 7.

When there is just one phenanthrene molecule in the complex we expect to see the ${}^1L_b$ band shifted slightly to lower energies,[3,4] and the extinction coefficient deduced from C_{11} and C_{12} conform to this, being very close to the extinction coefficient of the first band in the uncomplexed phenanthrene spectrum ($\varepsilon = 220$). The peak at 350 nm does not dominate the spectrum until the ratio $C_{12} : C_{11}$ is of the order of 1. It appears from a detailed examination of the spectrum in the 340—350 nm region that the 1 : 1 complex has a peak which is little shifted from that of the uncomplexed phenanthrene at 345 nm. In other words, it is only on addition of the second silver ion that there is a substantial shift of the ${}^1L_b$ band to lower energies. This is in accord with data for the Ag^+–benzene complex, for which no shift of the ${}^1L_b$ band was found.[3]

For the series (b), in which the concentration of Ag^+ is low and that of phenanthrene is increased, we deduce that there is a significant concentration of the 2 : 1 complex. The data for this series cannot be fitted well if such a complex is ignored. The fit of the data from series (*c*), which includes solutions having high Ag^+ concentrations, is as good as that for the other two series.

We have fewer data on the peak at 330 nm. Taking the equilibrium constants deduced from the above analysis we find extinction coefficients at 330 nm to be $\varepsilon_{11} = 410$, $\varepsilon_{12} = 580$, and $\varepsilon_{21} = 1800$. The standard deviation on 16 points is a factor of 20 worse than that obtained from the 350 nm set. However we were unable to improve this significantly by changing the equilibrium constants, and we believe the poorer fit is due to the lower accuracy of the measurements in this region.

We also carried out a series of measurements on the spectra at 300 nm. This is a more difficult region in which to obtain accurate intensities because there is no distinct maximum in the spectrum. On a series of 26 measurements, the K values determined earlier gave optimum extinction coefficients of $\varepsilon_{11} = 3800$, $\varepsilon_{12} = 7800$, and $\varepsilon_{21} = 2400$, and a standard deviation of $8{\cdot}7 \times 10^{-2}$. Although this is 25 times worse than the fit for the longer wavelengths it is not relatively much worse, as the optical densities are about 100 times larger in this region. However, optimum values of K were obtained from these data of

K_{11}	K_{12}	K_{21}
$1{\cdot}47 \times 10^3$ l mol^{-1}	$7{\cdot}95 \times 10^5$ l^2 mol^{-2}	$8{\cdot}75 \times 10^4$ l^2 mol^{-2}

which are appreciably different from those determined in the long wave region. Because we find that these K values give unreasonably large extinction coefficients when applied to the data from 350 nm, we believe they are a result of our measurements being made on the edge of an absorption band. If there is a small shift in the position of the ${}^1L_a$ band of phenanthrene with the nature of the medium, it will seriously influence our measurements.

In conclusion we believe that the optical measurements confirm the fact that the equilibrium between silver ion and phenanthrene is complex. We have obtained equilibrium constants which give a good fit to the intensity measurements at 350 nm and which give reasonable values for the extinction coefficients in this region. These extinction coefficients are in line with those expected on theoretical grounds. Because there are at least three complexes absorbing in the region studied, and conditions cannot be established to observe each independently, the data we have are insufficient to enable us to determine complete spectra for each of the three complexes. In the absence of such spectra we feel that we are unable to reach any further conclusions regarding the geometry of the complexes.

EXPERIMENTAL

Preparation of Materials.—(i) *Phenanthrene*. A good commercial sample was initially treated as described by Cohen and Cormier,[5] and finally purified by passage of a solution in n-hexane over activated alumina (see below), to give material of m.p. 100·0—100·5°. The u.v. spectrum showed that anthracene was absent.

(ii) [9-^{3}H]*Phenanthrene*. 9-Bromophenanthrene (51·4 g, 0·20 mol), m.p. 64°, prepared by bromination of phenanthrene and recrystallized from ethanol was added to magnesium turnings (5·4 g, 0·22 g-atom) in ether (15 ml) and benzene (15 ml). The mixture was refluxed for 8 h and then cooled; the mixture was treated with tritiated water (3·6 ml, 7 mCi ml^{-1}) followed by an excess of distilled water. The organic layer was separated, washed, and dried, and the solvent was distilled off. The residue was dissolved in light petroleum, b.p. 60—80°, and the solution was passed through an alumina column (50 × 15 cm, Type H, 100—200 mesh) and then evaporated to give [9-^{3}H]phenanthrene (32 g, 89%), m.p. 100—100·5°.

(iii) *Trifluoroacetic acid for rate and spectroscopic studies*. A commercial sample, (B.D.H. Ltd., Reagent Grade) (500 ml) was purified by fractional distillation first from silver oxide (5 g) and then from concentrated sulphuric acid (50 ml).

(iv) *Sodium and lithium trifluoroacetate*. An aqueous solution of analytical grade sodium or lithium carbonate was added to an excess of trifluoroacetic acid which had been distilled from silver oxide. The mixture was set aside overnight and then the solvents were removed under reduced pressure; the residue was dried under reduced pressure with warming.

Solutions of the salts in trifluoroacetic acid were prepared under dry nitrogen.

(v) *Silver trifluoroacetate*. Trifluoroacetic acid, distilled from silver oxide, was added slowly to warmed stirred suspension of silver carbonate in water until the mixture was neutral to litmus. The solution was filtered, and the filtrate was evaporated to dryness under reduced pressure with protection from the light. The residue was twice crystallised from anhydrous ether, and dried under reduced pressure in a drying pistol (P_2O_5).

Rate Studies.—The general method has been described

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[5] F. L. Cohen and U. Cormier, *J. Amer. Chem. Soc.*, 1930, **52**, 4363.

previously.[6] Sealed tubes were used for the reaction samples, an I.D.L. Tritium Scintillation Counter Type 6012A was employed, and a solution of 2,5-bis-[5-t-butylbenzoxazol-2-yl]thiophen in toluene (4 g l^{-1}) was used as the scintillator.

Good first-order kinetics were observed.

Spectroscopic Studies.—Measurements were made at room temperature (20° ± 1°) with a Unicam SP 500 spectrometer at fixed wavelength or with a Carey 14 spectrometer.

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[6] A. R. Butler and C. Eaborn, *J. Chem. Soc.* (*B*), 1968, 370, and references therein.