

10^7 l mol^{-1}) had been found to be comparable in magnitude to that of the Br_3^- ion, so that the halogen was completely complexed even by only a two-fold excess of amine. This c.t.c., whose u.v. spectrum is hypsochromically and hyperchromically shifted relative to that of free Br_2 , underwent a fast unimolecular reaction, consisting of an internal oxidation-reduction not involving the excess of free amine in the transition state, to give the products of equation (1).

In the case of tribenzylamine, the initial absorbance of its reaction mixture with bromine was much lower than that observed under the same conditions with triethylamine, although still higher than that expected for completely uncomplexed bromine. The early stage of the reaction involved a fast increase of the absorbance, which reached a maximum and then decayed to zero at a much slower rate. Furthermore, both the initial absorbance and the rates both in the rising and in the descending part of the kinetic curves increased with increasing amine concentration, as shown in Figure 1 (curves 2–4).

All these facts are consistent with the involvement of a tribenzylamine- Br_2 c.t.c. in the oxidative cleavage of this amine, as shown in the Scheme, provided that this complex had an u.v. absorption similar to that of the corresponding triethylamine- Br_2 c.t.c. (i.e. hypsochromically and hyperchromically shifted with respect to free Br_2), but a much lower K_f and a higher tendency to internal oxidation-reduction. With these hypotheses, increasing the amine concentration should produce a progressively more extensive complexation of the halogen and therefore a higher initial absorbance, as well as higher reaction rates.

The rising parts of the kinetic curves should correspond to the accumulation of the highly absorbing tribromide ion derived from the instantaneous capture of unreacted Br_2 by bromide salts (4) and (5) formed according to equation (3). The descending part of the same curves should then be due to the disappearance of Br_3^- , consumed at a much slower rate in the oxidative cleavage of the amine after all excess of free Br_2 has been used up.

Formation Constant of the Tribenzylamine- Br_2 C.t.c.—An attempt at the evaluation of the stoichiometry and formation constant of the supposed transient tribenzylamine- Br_2 c.t.c. was made with the method recently employed for the determination of K_f of a highly reactive olefin- Br_2 c.t.c.²⁰ In this method the transient charge-transfer absorbances (A°) were measured immediately after mixing amine and Br_2 solutions in the stopped-flow instrument. The A° values registered at 350 nm and 25 °C for an appropriate set of reaction mixtures are listed in Table 1. Preliminary estimates of the formation constant (K_f) and of the molar absorptivity (ϵ) of the c.t.c. were first obtained by ignoring the small contribution given to A° by free Br_2 and fitting the A° and initial concentration values to the Scott equation for 1:1 complexes²¹ (Figure 2). This fitting gave K_f 13.5 l mol^{-1} , ϵ 1 100 $\text{l mol}^{-1} \text{ cm}^{-1}$. These estimates were then used as starting parameters in a non-linear least-squares fitting procedure²⁰ also taking into account the free Br_2 absorption. The following final values were so obtained: K_f 9.7(1.0) l mol^{-1} , ϵ 1 300(90) $\text{l mol}^{-1} \text{ cm}^{-1}$. Both fittings were consistent with a 1:1 stoichiometry for the amine- Br_2 c.t.c. It can be observed that the individual K_f and ϵ values were not very well defined, as shown by their relatively high correlation coefficient ($r = -0.985$).^{*} Furthermore, some of the A° values reported

* r Stands for the total correlation coefficient between two given parameters, and is not to be confused with the more commonly quoted linear correlation coefficient between variables. The value of r is in the $(-1, +1)$ interval by definition. The value quoted here is high enough to state that K_f and ϵ are interdependent to some degree.

Table 1. Formation constant and molar absorptivity of the 1:1 tribenzylamine- Br_2 c.t.c. from initial absorbances at 350 nm of solutions of Br_2 and tribenzylamine (Am) in 1,2-dichloroethane at 25 °C

$10^4[\text{Br}_2]^a/\text{M}$	$10^2[\text{Am}]^b/\text{M}$	A° (2-cm cell)	$K_f^c/\text{l mol}^{-1}$	$\epsilon^c/\text{l mol}^{-1} \text{ cm}^{-1}$
5.6	10.3	0.73		
5.6	7.7	0.62		
5.6	5.2	0.51		
5.6	2.1	0.27		
4.6	4.9	0.39		
4.6	2.9	0.29		
4.6	1.95	0.22		
4.6	0.98	0.12		
2.8	2.10	0.13		
			9.7(1.0)	1 300(90)

^a At 350 nm $\epsilon_{\text{Br}_2} = 33 \text{ l mol}^{-1} \text{ cm}^{-1}$. ^b Tribenzylamine does not absorb at 350 nm. ^c Correlation coefficient: $r(K_f, \epsilon) = -0.985$.

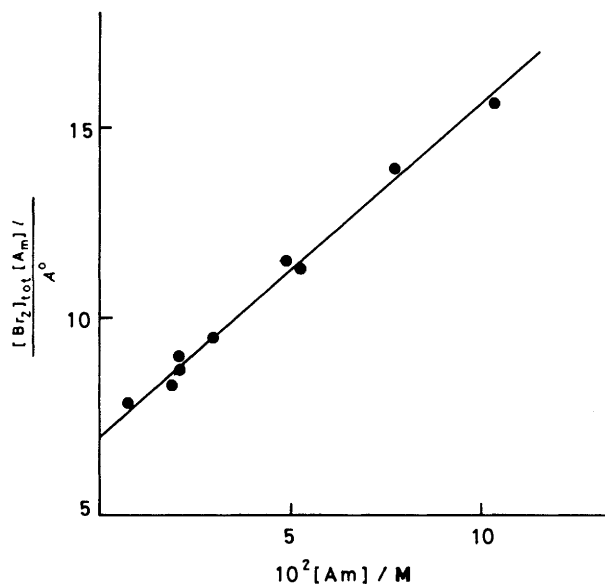


Figure 2. Scott plot of the absorbances (at 350 nm) and reagent concentrations for tribenzylamine (Am) and Br_2 mixtures in 1,2-dichloroethane at 25 °C

in Table 1 could have been overevaluated, especially those measured at the highest reagent concentrations, where the initial increase in absorbance was very fast. For this reason the product of the K_f and ϵ values so obtained is probably to be taken as the highest estimate for the product of the actual values of the two parameters.

Formation Constant of the Br_3^- Ion.—A quantitative treatment of the kinetic curves reported in Figure 1 for the reaction of tribenzylamine with bromine was complicated by the fact that, besides reaction (3) (Scheme), three equilibria, (2), (4), and (5), are involved, all of which contribute to the absorbance of the reaction mixtures. Moreover, direct reaction of the excess of amine with the formed tribromide ion could not be excluded *a priori*. A further complication arose since the formation constant of the Br_3^- ion in a given solvent depends on the counterion.²² For instance, K_f values of 9×10^4 and $2 \times 10^2 \text{ l mol}^{-1}$ have been respectively reported²³ for tetrabutylammonium tribromide and pyridinium tribromide in chloroform at 25 °C. Different values of K_f were therefore to be

Table 2. Formation constant and molar absorptivities of tribenzylammonium tribromide from absorbances at 340, 350, 360, and 410 nm of solutions of Br₂ and tribenzylammonium tribromide (AmHBr) in 1,2-dichloroethane at 25 °C

10 ⁴ [Br ₂] ^a /M	10 ⁴ [AmHBr] ^b /M	Absorbances (1 cm optical path) at (nm)				
		340	350	360	410	
1.0	1.05	0.060 ^c	0.038 ^c	0.028 ^c	0.021 ^c	
2.0	2.1	0.20	0.13	0.10	0.06	
4.0	4.2	0.525	0.335	0.22	0.135	
4.85	6.85	0.90	0.58	0.39	0.185	
4.85	10.25	1.00	0.68	0.45	0.20	
4.85	13.7	1.17	0.77	0.50	0.22	
4.85	34.0	1.50	0.985	0.635	0.25	
4.85	52.0	1.55	1.035	0.672	0.255	
4.85	102.5	1.64	1.12	0.735	0.27	
4.85	205	1.66	1.15	0.75	0.275	
4.85	505	1.70	1.19	0.765	0.306	
5.0	5.2	0.82	0.525	0.38	0.21	
5.0	26.1	1.485	0.96	0.635	0.25	
	<i>K_f</i>	2 220(340)	2 200(320)	2 530(510)	2 300(630)	1 mol ⁻¹
	ϵ	3 700(320)	2 330(160)	1 470(100)	570(20)	1 mol ⁻¹ cm ⁻¹ ^d
	overall <i>K_f</i> (see text)			2 300(75)		1 mol ⁻¹

^a ϵ_{Br_2} was 20, 33, 65, and 211 l mol⁻¹ cm⁻¹ at 340, 350, 360, and 410 nm, respectively. ^b The absorbance values were corrected, when necessary, for a small contribution from AmHBr. ^c Measured in a 5-cm cell. ^d Values of ϵ for tetrabutylammonium tribromide in 1,2-dichloroethane: 3 850, 2 500, 1 680, and 530 l mol⁻¹ cm⁻¹ at 340, 350, 360, and 410 nm, respectively.⁸

expected for the Br₃⁻ ion in *NN*-dibenzylbenzylidenammonium tribromide and in tribenzylammonium tribromide, which in the solvent used are certainly present as more or less tight ion pairs.

Equilibrium (5) was easily investigated by spectrophotometric measurement of mixtures of bromine and tribenzylammonium bromide in 1,2-dichloroethane at 25 °C (Table 2). The method of Rose and Drago,²⁴ used successfully for the determination of *K_f* of pyridine tribromide in chloroform,²³ was not suitable in the present case because of the higher value of the formation constant. The latter was best obtained by the recently reported²⁰ non-linear least-squares fitting procedure, using as starting values for ϵ and *K_f* those evaluated assuming that Br₂ was completely transformed into Br₃⁻ at the highest tribenzylammonium bromide concentration of Table 2. The *K_f* and ϵ values obtained at several wavelengths are listed in Table 2. It can be observed that these molar extinction coefficients are very similar to those of tetrabutylammonium tribromide both in 1,2-dichloroethane and in chloroform and of pyridinium tribromide in chloroform.²³ This confirms that the cation and the solvent have a much larger effect on the stability of ammonium tribromides than on their absorptivities. A final calculation using simultaneously the absorbances measured at 340, 350, 360, and 410 nm gave *K_f* 2.30(0.07) × 10³ l mol⁻¹ for tribenzylammonium tribromide. For this fitting the values of the molar extinction coefficient were those previously determined for tribenzylammonium tribromide at each wavelength. The reported standard deviation is presumably somewhat optimistic, due to this approximation.

Equilibrium (4) was awkward to investigate because of the difficulty of obtaining the pure bromide (4) and its high sensitivity to moisture. The *K_f* values of Br₃⁻ in this salt could not be obtained.

Rate Constants and Mechanisms.—Unfortunately the above failure, as well as the low *K_f* value found for Br₃⁻ in tribenzylammonium tribromide, did not allow steps (4) and (5) in the Scheme to be treated as instantaneous, practically non-equilibrium processes withdrawing an amount of free Br₂ equal to that of the bromide ion formed in the oxidation–reduction reaction. The approximations applied successfully to the kinetic

treatment of a somewhat similar case, where bromide ions were formed during a bromination reaction,^{8a} were therefore inapplicable to the present case.

It was therefore impossible to obtain values of the rate constant for the investigated reaction from kinetic curves of the type shown in Figure 1. The problem was, however, solved by using as oxidizing reagent, in place of molecular Br₂, a pre-formed tribromide salt endowed with a very high formation constant for the Br₃⁻ ion. Tetrabutylammonium tribromide (TBAT), *K_f* ≥ 2 × 10⁷ l mol⁻¹ in 1,2-dichloroethane,⁸ was generated from Br₂ and excess of tetrabutylammonium bromide (TBAB) and reacted with excess of tribenzylamine in this solvent at 25 °C. The reaction was followed spectrophotometrically by monitoring the disappearance of the Br₃⁻ ion at 380 nm. Regularly decreasing absorbance–time curves were thus obtained; they obeyed very cleanly, up to over 90% conversion, the overall second-order rate law (6) (where Am is tribenzylamine).

$$-d[\text{Br}_3^-]/dt = k_{2\text{obs}} [\text{Br}_3^-][\text{Am}] \quad (6)$$

Assuming that both a Br₃⁻ and a free Br₂ process, with respective rate constants *k_{2Br₃}*⁻ and *k_{2Br₂}*⁻, are actually operating in these reactions with the amine, a rate law of the type (7) would be expected.

$$-d[\text{Br}_2]_{\text{tot}}/dt = (k_{2\text{Br}_2}[\text{Br}_2]_{\text{free}} + k_{2\text{Br}_3}[\text{Br}_3^-])[\text{Am}] \quad (7)$$

$$[\text{Br}_2]_{\text{tot}} = [\text{Br}_2]_{\text{free}} + [\text{Br}_3^-] \quad (8)$$

$$[\text{Br}_2]_{\text{free}} = [\text{Br}_3^-]/K_f[\text{Br}^-] \quad (9)$$

$$-d[\text{Br}_3^-]/dt = \{K_f[\text{Br}^-]/(1 + K_f[\text{Br}^-])\} \{(k_{2\text{Br}_2} + k_{2\text{Br}_3}K_f[\text{Br}^-])/K_f[\text{Br}^-]\} [\text{Br}_3^-][\text{Am}] \quad (10)$$

$$k_{2\text{obs}} = (k_{2\text{Br}_2} + k_{2\text{Br}_3}K_f[\text{Br}^-])/(1 + K_f[\text{Br}^-]) \quad (11)$$

$$k_{2\text{obs}} \cong (k_{2\text{Br}_2}/K_f[\text{Br}^-]) + k_{2\text{Br}_3} \quad (12)$$

Noting that the total Br₂ and the free Br₂ are given,

Table 3. Values of $k_{2\text{obs}}$ [equation (6)] for the reaction of tribenzylamine (Am) with tetrabutylammonium tribromide in the presence of excess of tetrabutylammonium bromide (TBAB) in 1,2-dichloroethane at 25 °C^a

$10^3[\text{TBAB}]/\text{M}$	$10^3[\text{Br}_2]/\text{M}$	$10[\text{Am}]/\text{M}$	$10^3k_{2\text{obs}}/\text{l mol}^{-1} \text{s}^{-1}$
6.8	1.38	1.16	8.33
13.5	1.38	1.16	3.46
20.4	1.56	1.95	2.20
30.1	1.38	1.16	1.78
47.2	1.38	1.16	1.26
80.0	1.44	1.14	0.91
119	1.38	1.16	0.69
150	1.44	1.14	0.66
192	1.56	1.95	0.50

^a The reactions were monitored at 380 nm.

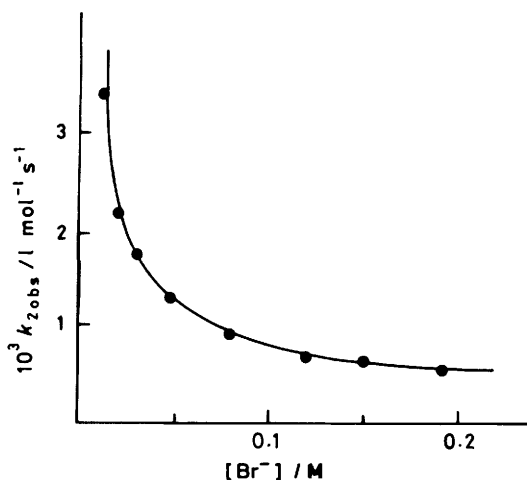
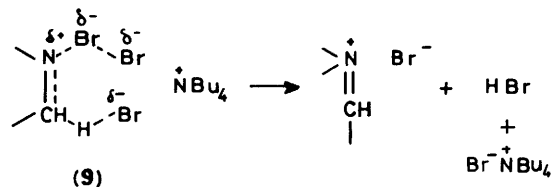
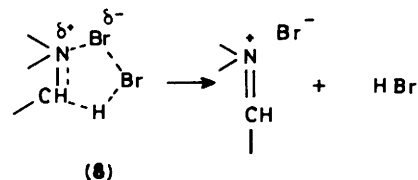


Figure 3. Plot of $k_{2\text{obs}}$ versus tetrabutylammonium bromide (TBAB) concentrations [equation (12)] for the reaction of tribenzylamine with tetrabutylammonium tribromide at 380 nm in 1,2-dichloroethane at 25 °C

respectively, by equations (8) and (9) (where K_f is the formation constant of the Br_3^- ion), equation (7) can be rearranged to (10), which is equivalent to the experimental relationship (6) provided that $k_{2\text{obs}}$ is given by equation (11). Since the formation constant of the employed tribromide is extremely high ($K_f \geq 2 \times 10^7 \text{ l mol}^{-1}$), equation (11) can be safely approximated by equation (12). The latter equation allows the values of $k_{2\text{Br}_2^-}$ and of $k_{2\text{Br}_2^-}/K_f$ to be obtained easily from the dependence of the observed second-order rate constant on the concentration of added TBAB.

The kinetic runs were carried out in the presence of an increasing excess of added TBAB. The $k_{2\text{obs}}$ values are given in Table 3. The fit of these data to equation (12) is shown in Figure 3. It must be stressed that, since only a limiting value can be given for K_f of the Br_3^- ion in TBAT, the same happens for $k_{2\text{Br}_2^-}$. The following values were thus obtained: $k_{2\text{Br}_2^-} 3.1(0.4) \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$, $k_{2\text{Br}_2^-}/K_f 4.45(0.3) \times 10^{-5} \text{ s}^{-1}$, and therefore $k_{2\text{Br}_2^-} \geq 8.9 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$.

The formation of a labile tribenzylamine- Br_2 c.t.c. from Br_2 and the amine having been demonstrated, its involvement in both the free Br_2 and in the Br_3^- reaction seemed very probable. Even if the formation constant of this c.t.c. is rather low, it can facilitate the transfer of a small fraction of Br_2 from the stable Br_3^- ion to tribenzylamine, thus allowing this reaction to occur



through the amine- Br_2 c.t.c. If this is true, the rate constant $k_{2\text{Br}_2^-}$ in equation (12) should be given by (13), where K_f and k_1

$$k_{2\text{Br}_2^-} = K_f k_1 \quad (13)$$

are respectively the formation constant of the c.t.c. and the rate constant for its unimolecular oxidation-reduction. Using the above determined value of this formation constant [$K_f 9.7(1.0) \text{ l mol}^{-1}$], a limiting estimate of $k_1 \geq 90 \text{ s}^{-1}$ can be obtained. This value is at least 50 times higher than that measured for the analogous reaction of the triethylamine- Br_2 c.t.c., in agreement with the expectation based on the higher acidity of the α -hydrogens in tribenzylamine relative to triethylamine, and with the qualitative interpretation of the kinetic curves of Figure 1.

It can also be stressed that the first-order dependence on the amine of both the Br_2 and the Br_3^- reactions also excludes the intervention of a second amine molecule, helping in proton abstraction from the c.t.c., and suggests a direct release of unionized HBr. The transition state of the former reaction can therefore be depicted as a cyclic five-membered species (8) of the type involved in the nitrosative cleavage of tertiary amines.¹⁹ Only subsequently is the eliminated HBr captured by the excess of amine.

For the Br_3^- reaction, it can be pointed out that the relative rate constant $k_{2\text{Br}_2^-}$, although small, is certainly well defined by the fitting of the rate data to equation (12), so that a concurrent Br_3^- process in the reaction with tribenzylamine appears to be firmly established. Although the mechanistic implications are not unambiguously defined by the present data, the latter process can reasonably be supposed to consist of a bromide ion-promoted elimination of HBr from the amine- Br_2 c.t.c., proceeding through a transition state of type (9), where one Br_2 molecule and one Br^- anion, or one Br_3^- ion, are simultaneously involved, and the tetrabutylammonium cation may help by ion-pair formation to a leaving bromide.

Conclusions

The results of the present investigation definitely disprove the isolation of a solid tribenzylamine- Br_2 adduct of type (1). Spectral evidence for the transient formation of a 1:1 c.t.c. has been obtained from the stopped-flow technique, but this species is certainly very unstable, its formation constant being lower by at least six orders of magnitude than that of the highly stable 1:1 triethylamine- Br_2 c.t.c.¹⁶ This is not surprising in view of the large difference in $\text{p}K_a$ between these two amines in a low polarity, non-protic solvent: for example, in chloroform $\Delta\text{p}K_a > 4.2$.²⁵ An extra decrease in entropy associated with a

considerable loss of rotational freedom of the three benzyl substituents, due to the proximity of the large bromine molecule to the amine nitrogen in the c.t.c., is probably an additional destabilizing factor for the complex. Furthermore, the tribenzylamine-Br₂ c.t.c. undergoes internal oxidation-reduction to iminium and bromide ions at a rate at least 50-fold higher than that of the highly reactive triethylamine-Br₂ analogue. This makes even more problematic the isolation of such an unstable species.

It can finally be observed that similar behaviour seems to be general for systems consisting of tertiary amines bearing non-aromatic nitrogen substituents and bromine, with the possible exception of trimethylamine and of bridgehead nitrogen amines of the quinuclidine type, which give stable complexes with bromine since C=N double-bond formation would violate Bredt's rule.²⁶

Experimental

Materials and Methods.—Carbon tetrachloride was refluxed over P₂O₅ before use. 1,2-Dichloroethane was treated as previously reported.⁸ Best quality commercial bromine (C. Erba RPE > 99.5%) was kept in 1 ml sealed vials and opened immediately before use without further purification. Tribenzylamine (Fluka; ca. 99%) was crystallized from hexane and stored under argon. Tetrabutylammonium bromide (EGA; ca. 99%) was crystallized from ethyl acetate-benzene. Tribenzylammonium tribromide was obtained from the amine and gaseous HBr in CCl₄ and was crystallized from 7:3 CCl₄-CHCl₃.

I.r. spectra of Nujol mulls were taken on a Pye-Unicam SP3-300 spectrophotometer. U.v. spectra were recorded on a Pye-Unicam SP8-400 u.v.-visible spectrophotometer. ¹H N.m.r. spectra were taken on a Varian CFT-20 instrument operating at 80 MHz. Kinetic measurements were performed either on a Durrum D-110 stopped-flow apparatus or on the u.v.-visible spectrophotometer equipped with a thermostatted cell-holder.

All calculations were carried out with BASIC programs running on a Commodore 4032 personal computer.

Preparative Reaction of Tribenzylamine with Br₂.—A 0.35M solution of tribenzylamine in CCl₄ (10 ml) was added dropwise under stirring to an equimolar amount of Br₂ in the same solvent (10 ml) at -25 °C. The yellow solid which immediately precipitated was rapidly collected and its i.r. (Nujol mull), u.v. (CH₃CN), and n.m.r. (CD₃CN) spectra were taken (Found: C, 48.2; H, 4.0; N, 2.6; Br, 44.9. Calc. for a 1:1 mixture of C₂₁H₂₀Br₃N and C₂₁H₂₂Br₃N: C, 47.85; H, 4.0; N, 2.65; Br, 45.5%). The same product was obtained by adding Br₂ to the amine solution.

Kinetic Measurements.—(a) *Reaction of tribenzylamine with Br₂.* Stock solutions of Br₂ in 1,2-dichloroethane were prepared and stored under protection from external light. Concentrations were determined from the u.v. spectra.⁸ These solutions were checked from time to time for the absence of Br₃⁻ ions (deriving from the reaction of Br₂ with HBr possibly present in the solution)⁸ by measuring the u.v. absorption in the 280–350 nm range, where the absorption minimum of Br₂ occurs, and discarded when the molar extinction coefficients at 287 and 350 nm exceeded those of Br₂ (35 and 33 l mol⁻¹ cm⁻¹, respectively).

The Durrum stopped-flow instrument, equipped with a 2 cm observation cell, had a mixing time of 3 ms. It was coupled to a Tektronix 5103 storage oscilloscope and to a data acquisition system built around a 12-bit A/D converter, interfaced to a Commodore 4032 personal computer. Temperature control

inside the observation cell (±0.1 °C) was achieved with a Lauda MK 70 constant-temperature circulating bath.

The reactions were monitored at 350 nm, where tribenzylamine does not absorb and Br₂ has a low molar extinction coefficient (ε 33 l mol⁻¹ cm⁻¹). The highest data acquisition rate available (10⁴ data points s⁻¹) was used during the first 10 ms of reaction, and the absorbances measured immediately after the dead time, at the reagent concentrations of Table 1, were taken as the initial absorbance values. A few absorbance-time curves are shown in Figure 1.

(b) *Reactions of tribenzylamine with tetrabutylammonium tribromide.* Tetrabutylammonium bromide was dissolved in Br₂ solutions in 1,2-dichloroethane at the concentrations shown in Table 3. The u.v. spectra of the resulting solutions showed a Br₃⁻ concentration exactly equal to that of total initial Br₂. These solutions were prethermostatted at 25 °C and mixed with equal volumes of tribenzylamine solutions in the same solvent. The reactions were followed by monitoring the disappearance of Br₃⁻ at 380 nm on the u.v.-visible spectrophotometer.

The *k*_{2obs} values for this reaction were fitted to equation (12) by a weighted least-squares procedure. Different weights had to be used since the estimated standard deviation on the *k*_{2obs} values was found to be ca. 5% of *k*_{2obs}. Therefore it varied, in absolute terms, by more than an order of magnitude over the experimental values (Table 3). Furthermore, the propagation of error from the measured amount of Br⁻ (conservatively estimated as 1 mg) to *k*_{2obs} was quite different over the range of Br⁻ measured, owing to the hyperbolic function (12). The weight of each experimental point was then taken as proportional to the inverse of the estimated variance, according to established formulae.²⁷

Formation Constant of the Tribenzylamine-Bromine C.t.c.—The formation constant *K*_f is given by equation (14) where *x* is

$$K_f = x / \{ ([Am]_{tot} - x)([Br_2]_{tot} - x) \} \quad (14)$$

the concentration of the c.t.c. formed, Br₂ is the acceptor (bromine), and Am is the donor (tribenzylamine). An acceptable solution is the smallest one [equation (15)].

$$x = 0.5([Am]_{tot} + [Br_2]_{tot} + 1/K_f) - \{ 0.25([Am]_{tot} + [Br_2]_{tot} + 1/K_f)^2 - [Br_2]_{tot}[Am]_{tot} \}^{1/2} \quad (15)$$

The initial transmittance (*T*^o) of tribenzylamine-bromine mixtures, at wavelengths where the amine is transparent, is given by equation (16) where [Br₂]_{tot} is the total initial con-

$$-\log(T^o) = \epsilon_{Br_2}([Br_2] - x) + \epsilon x \quad (16)$$

centration of bromine and ε is the molar absorptivity of the c.t.c. This equation implicitly contains *K*_f through the presence of *x*. It contains as measured variables the total concentrations and the transmittance; the fitting parameters are *K*_f and ε, whose starting values were obtained from the Scott plot of Figure 2. The calculated transmittance values were compared with the experimental ones by a non-linear least-squares fitting procedure (NLLSQ).²⁷

The correlation coefficient between *K*_f and ε was ca. -0.985. This relatively high value is due to the limited complexation range of acceptor (8–48% for the data of Table 1). However, higher concentrations of tribenzylamine were avoided because of the excessive increase of the initial reaction rate.

Formation Constant of Tribenzylammonium Tribromide.—The absorptions of solutions of Br₂ and tribenzylammonium tribromide at the concentrations of Table 2 in 1,2-dichloro-

ethane at 25 °C were measured in the 340–410 nm range. The formation constant and molar absorptivities of Br_3^- at each wavelength were calculated with the NLLSQ procedure using equations similar to (14)–(16), where the concentration of tribenzylammonium tribromide was introduced in place of that of the free amine and ϵ of Br_3^- in place of ϵ of the amine· Br_2 c.t.c. K_f and ϵ were the fitting parameters.

Acknowledgements

This work was supported by a grant from the Consiglio Nazionale delle Ricerche and from the Ministero della Pubblica Istruzione.

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Received 6th January 1986; Paper 6/050