

Electron Transfer Reactions in Organic Chemistry XVI.* The Reduction of Carbon Tetrabromide and some other Polyhaloalkanes by *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine

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The reaction between CBr_4 and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPDA) has been studied in acetonitrile at 20 and 50°C. The formation of $\text{TMPDA}^{+\cdot}$ was found to be first order in both $[\text{TMPDA}]$ and $[\text{CBr}_4]$, while its disappearance was first order in $[\text{TMPDA}^{+\cdot}]$ but zeroth order in $[\text{CBr}_4]$. The rate constants at 50°C were $6.5 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$ and $5 \times 10^{-5} \text{ s}^{-1}$, respectively. The only products detected were carbon monoxide, bromide ion and acid.

The following mechanism is proposed: TMPDA reduces CBr_4 in an initial electron-transfer step to form $\text{TMPDA}^{+\cdot}$, $\text{Br}_3\text{C}^\cdot$ and Br^- . The radical couples with oxygen to form the tribromomethylperoxyl radical, which is further reduced to the anion by another molecule of TMPDA. CBr_3OO^- then forms CO, Br^- and H^+ , probably by hydrolysis. CBrCl_3 and CBr_2Cl_2 are proposed to react with TMPDA by the same mechanism, while $(\text{CBrCl}_2)_2$ reacts by another mechanism. The reaction rates with CHBr_3 and C_2Cl_6 were too slow to be measurable. The order of reactivity is $\text{CBr}_4 > \text{CBr}_2\text{Cl}_2 > \text{CBrCl}_3 \gg (\text{C}_2\text{Cl}_6 \text{ and } \text{CHBr}_3)$.

It has long been known that amines form charge-transfer (CT) complexes with polyhalogenated alkanes (PHA)¹ and that these are photochemically unstable. Thus the reaction between carbon tetrachloride and amines² irradiated with UV light has been shown to form products which were attributed to photochemical decomposition of the CT complex via an initial charge transfer. Kender³ found that tributylamine and CCl_4 also reacted in the absence of light, and he argued that the reaction proceeded through an initial electron transfer (ET) from the amine to the haloalkane. Enamines⁴ and a ketene aminal⁵ have also been claimed to react with PHAs according to an ET mechanism. On the other hand a polar mechanism was considered⁶ for the reaction between PHAs and tetrakis(dimethylamino)ethylene (TDAE). This is somewhat surprising because TDAE has an estimated E° of -0.5 V vs. the normal hydrogen electrode (all potentials will be referred to this electrode in the following), while ordinary amines and enamines have approximate E° values which are at least 1 V higher.⁷

While reductions with TDAE⁸ have in most cases been described as two-electron reactions, probably because the radical cation of TDAE is readily oxidized to the corresponding dication, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPDA) is a well known ET-reducing agent,^{7,9} with $E^\circ = 0.24 \text{ V}$ in acetonitrile (AN).¹⁰ The radical cation

of TMPDA, also known as Wurster's blue, is rather stable with $E^\circ = 0.82 \text{ V}$ for its further oxidation to the dication.¹⁰ $\text{TMPDA}^{+\cdot}$ shows two strong absorption bands at 610 and 560 nm,⁷ making it easy to monitor its formation and disappearance. TMPDA therefore appears to be well suited as a reductant in a study of a putative ET reaction between amines and PHAs.

CT complexes between PHAs and TMPDA have been described,¹¹ but to the best of our knowledge the direct reaction between simple PHAs and TMPDA has not been previously studied. However, in reactions between TMPDA and hexafluoro- and hexachloro-acetone,¹² and difluorodinitromethane,¹³ ET mechanisms have been proposed. Sosonkin *et al.*,¹⁴ also reported an ET reaction between TMPDA and CCl_4 , mediated by benzoquinone.

The reaction between TMPDA and PHAs is a logical extension of our previous studies,¹⁵ where we treated PHAs with cobalt(II)sepulchrate²⁺ and the heteropoly blue $\text{Co(II)W}_{12}\text{O}_{40}^{7-}$. These outer-sphere ET reagents reduced CX_4 and C_2X_6 ($\text{X} = \text{Cl}, \text{Br}$) by an initial ET, thus forming a halide ion and a perhaloalkyl radical, which was further reduced to the anion by another molecule of reductant. In the case of polyhalomethanes the anion was protonated by the solvent (AN–water), while the anions from polyhaloethanes eliminated a halide ion, forming polyhaloethylenes. The intermediacy of the radical was indicated by formation of the corresponding coupling product and/or by trapping it with *N*-*t*-butyl- α -phenylnitron (PBN) and detection of the spin adduct by ESR spectroscopy.

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Table 1. Products from the reaction between CBr₄ and TMPDA in AN at 50 °C. The reaction time was 65 h.

Starting concentrations/mmol l ⁻¹			Final concentrations/mmol l ⁻¹				
CBr ₄	TMPDA	TRIS ^a	CBr ₄	Br ⁻	CHBr ₃	Br _{tot} ^b	H ⁺
10	10	0	7.0	10	0	38	9
10	20	0	5.7	15	0	38	c
5	20	0	1.3	21	0	26	c
10	10	40	0	39	1.0	42	>35
10	1.3	40	3.2	23	0.4	37	c
10	0	40	9.7	3	0.3	43	0

^aAll runs with TRIS were carried out in AN–water (90:10 v/v). ^bBr_{tot} = [CBr₄]×4 + [CHBr₃]×3 + [Br⁻]. ^cNo data.

Results

Unbuffered runs. (a) Product studies. When the reactants were mixed the solution turned yellow due to the formation of the CT complex between CBr₄ and TMPDA. The yellow colour was slowly mixed with the blue colour from TMPDA⁺ and, after a while, the solution became deep blue. On completion of the reaction the solution was red-dish-brown. The results and conditions for non-deaerated* runs from GLC, ion chromatography (IC), pH measurements and FT-IR are summarized in Tables 1 and 2. No volatile products were found and only CBr₄ and TMPDA were detected by GLC (OV-101 column, 290 °C, 60 min). It can be seen in Table 1 that almost 4 mol of TMPDA (initially present) were needed to consume 1 mol of CBr₄, and that almost 4 mol of Br⁻ were formed per mol of consumed CBr₄. pH Measurements showed that acid was formed and by taking out aliquots during the early stages of the reaction, it was shown that a considerable part of this was formed during the formation of TMPDA⁺. The final concentrations of acid and Br⁻ were approximately equal. It is important to note that the addition of stoichiometric amounts of acid to the solutions completely inhibited the

* [O₂] was estimated to be 2 mmol l⁻¹ in air-saturated and 10 mmol l⁻¹ in O₂ saturated AN.¹⁶

reaction, thereby showing that TMPDAH⁺ was unreactive. Carbon monoxide was formed in significant amounts but no CO₂ was found except for atmospheric CO₂ which somewhat hampered the analysis (Table 2). It must be stressed that the gas-sampling technique was rather primitive and that the yields in Table 2 must be regarded as semiquantitative.

When the reactions were carried out in deaerated solutions, less CO was formed, but acid was formed and no volatile products were found by GLC.

Only a few product runs were carried out with CBrCl₃ as the substrate. No CHCl₃ or C₂Cl₆ was found by GLC, but the same amount of acid was formed as in the reactions

Table 2. Approximate yield of CO. The reaction time was 5 h.

Starting concentrations			Yield [CO]/mmol l ⁻¹
[TMPDA]/mmol l ⁻¹	[CBr ₄]/mmol l ⁻¹	[O ₂]/mmol l ⁻¹	
20	200	10 ^a	2
20	200	2 ^b	2
20	200	0 ^c	0.2

^aBubbled with O₂. ^bAir-saturated. ^cBubbled with Ar.

Table 3. Rate constants for the reactions with TMPDA. The estimated experimental errors are ± 10–20 % for k₁ and ± 25–50 % for k₂. [TMPDA]₀ = 0.0476 mmol l⁻¹, unless otherwise stated.

Substrate	Conc/mol l ⁻¹	T/°C	Calc. method ^a	k ₁ /10 ⁻⁴ l mol ⁻¹ s ⁻¹	Calc. method ^a	k ₂ /10 ⁻⁵ s ⁻¹
CBr ₄	0.10–0.80	50	2	7.5	1	5
CBr ₄	0.10	50	3	6.5	–	–
CBr ₄	0.80	20	2 ^b	0.60	2 ^b	0.03
CBr ₄ ^c	0.050–0.80	20	2	0.40	–	–
CBr ₄ ^d	0.010	50	2	10	2	4
CBr ₂ Cl ₂	0.40	50	3	3.1	2	6
CBrCl ₃	0.97	50	3	0.75	2	4
C ₂ Cl ₆	0.20	50	No reaction			
CHBr ₃	0.90	50	No reaction			

^a1 = eqn. (1); 2 = eqn. (2); 3 = initial rates. ^bε (TMPDA, 611 nm) = 11000 l mol⁻¹ cm⁻¹ was used to obtain a good fit for the descending part of the curve. ^c[TMPDA]₀ = 0.024–0.38 mmol l⁻¹. ^d[TMPDA]₀ = 5.0 mmol l⁻¹.

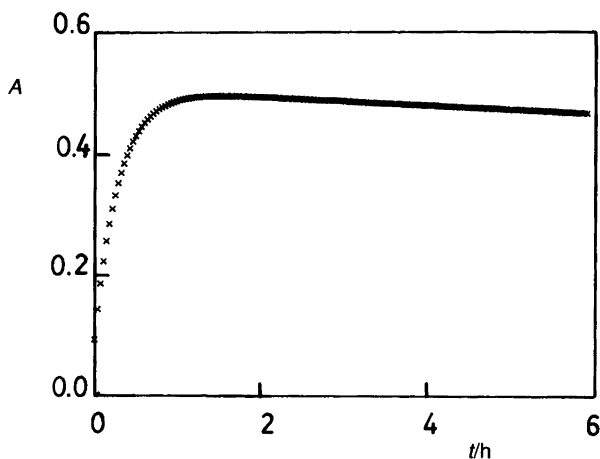


Fig. 1. Plot of absorbance at 611 nm vs. time for the reaction between TMPDA (0.048 mmol l⁻¹) and CBr₄ (0.80 mol l⁻¹) at 20°C.

with CBr₄. Yellow CT complexes were also formed with CBrCl₃, CBr₂Cl₂ and (CBrCl₂)₂.

(b) *Kinetics.* The experimental conditions and the calculated rate constants are found in Table 3, but before we discuss how the rate constants were calculated it seems appropriate that a general description of the kinetic curves is given. For the reaction between CBr₄ and TMPDA at 20°C in AN, a curve was obtained which fitted deceptively well to a first-order equation. Close inspection revealed that the radical cation slowly disappeared (Fig. 1), and that the maximum absorbance at 611 nm only corresponded to approximately 75% of that expected if all the TMPDA had been oxidized to TMPDA^{•+}. This biphasic behaviour became much more apparent when the reaction temperature was raised to 50°C (Fig. 2). The curves from the reactions with CBr₄, CBr₂Cl₂ and CBrCl₃ were similar, while the curve obtained for (CBrCl₂)₂ was clearly different (Fig. 3).

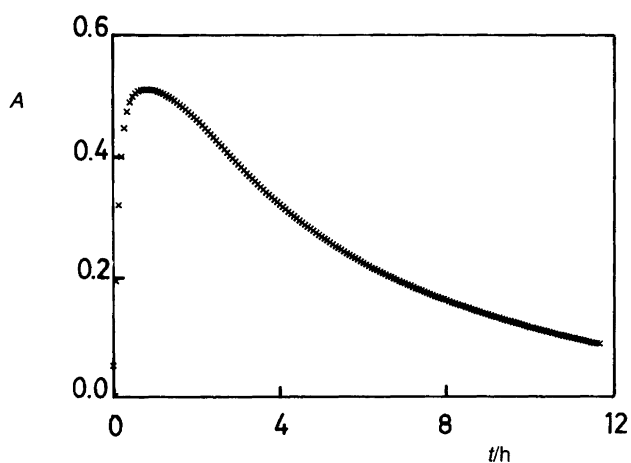


Fig. 2. Plot of absorbance at 611 nm vs. time for the reaction between TMPDA (0.048 mmol l⁻¹) and CBr₄ (0.80 mol l⁻¹) at 50°C.

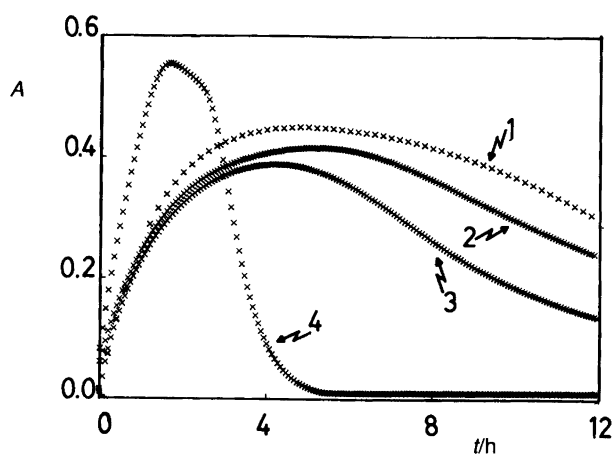


Fig. 3. Plot of absorbance at 611 nm vs. time for the following reactions with TMPDA (0.048 mol l⁻¹) at 50°C: 1, CBr₄ (0.10 mol l⁻¹); 2, CBr₂Cl₂ (0.40 mol l⁻¹); 3, CBrCl₃ (0.97 mol l⁻¹); 4, (CBrCl₂)₂ (0.20 mol l⁻¹).

Here the absorbance rose sharply, almost to the highest possible value, and then fell equally fast.

(c) *Kinetics with CBr₄.* The method of initial rates was considered to give the most reliable results for the calculation of the rate constant for the formation of TMPDA^{•+} (*k*₁), because of the influence of acid and other products on the rate of reaction. Only the part of the curve corresponding to *A* (absorbance) = 0.03–0.06 was used and the rates were calculated by linear regression. The correlation coefficient was always better than 0.999. The slopes of the plots of log[(*dA/dt*)/s⁻¹] vs. log([CBr₄]₀/mmol l⁻¹) and log([TMPDA]₀/10⁻⁶ mol l⁻¹) were 1.11 and 1.04 respectively, both with correlation coefficients equal to 0.999 (Fig. 4). ε(TMPDA^{•+}, 611 nm) = 12900 l mol⁻¹ cm⁻¹ was used¹⁷ to convert absorbance data into concentrations.

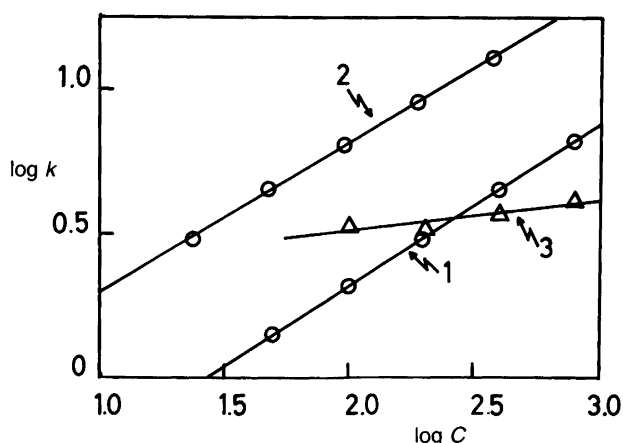


Fig. 4. Plots of log *k* vs. log *C*: 1, formation of TMPDA^{•+} at 20°C, [TMPDA]₀ = 0.048 mmol l⁻¹, *k* = (*dA/dt*)/10⁻⁶ s⁻¹, *C* = [CBr₄]₀/mmol l⁻¹; 2, formation of TMPDA^{•+} at 20°C, [CBr₄]₀ = 0.40 mol l⁻¹, *k* = (*dA/dt*)/10⁻⁶ s⁻¹, *C* = [TMPDA]₀/10⁻⁶ mol l⁻¹; 3, disappearance of TMPDA^{•+} at 50°C, [TMPDA]₀ = 0.048 mmol l⁻¹, *k* = *k*₂/10⁻⁵ s⁻¹, *C* = [CBr₄]₀/mmol l⁻¹.

The rate constant for the consumption of $\text{TMPDA}^{+\cdot}$ (k_2) at 50 °C was obtained from the descending part of the curve with $A < 0.3$, which could be fitted by the first-order eqn. (1) with A_∞ and k_{obs} as disposable parameters. A plot of $\log(k_{\text{obs}}/10^{-5} \text{ s}^{-1})$ vs. $\log([\text{CBr}_4]_0/\text{mmol l}^{-1})$ gave a slope of 0.13 and a correlation coefficient of 0.89 (Fig. 4).

$$A = A_\infty + (A_0 - A_\infty)\exp(-k_{\text{obs}}t) \quad (1)$$

The complete biphasic curve was analysed using eqn. (2),¹⁸ where k_1 and k_2 are the first-order rate constants for the formation and consumption of $\text{TMPDA}^{+\cdot}$. Thus the curve obtained at 50 °C with $[\text{CBr}_4]_0 = 0.8 \text{ mol l}^{-1}$ could be fitted by eqn. (2) and both k_1 and k_2 were almost within experimental error of those calculated by the previously described methods. When a lower $[\text{CBr}_4]_0$ was used the equa-

$$[\text{TMPDA}^{+\cdot}] = \frac{k_1[\text{TMPDA}]}{k_2 - k_1} [\exp(-k_1t) - \exp(-k_2t)] \quad (2)$$

tion could not be fitted to the curve. However k_2 at 20 °C was obtained by this method since the reaction was too slow for the rate to be obtained by eqn. (1). A few runs were carried out with concentrations similar to those in the product runs. Eqn. (2) fitted well and the rate constants were in good agreement with those for the other runs.

During efforts to increase the stability of $\text{TMPDA}^{+\cdot}$ it was found that added water (10 % by volume) increased k_1 by a factor of 1.7. The disappearance of $\text{TMPDA}^{+\cdot}$ was not studied, but the A_{max} obtained was the same as in the absence of water. Deaerating the solutions with Ar did not change the values of k_1 and k_2 .

(d) *Kinetics with the other substrates.* The kinetic curves obtained with CBr_2Cl_2 and CBrCl_3 as substrates could be fitted reasonably well by eqn. (2), and k_2 values were taken from these calculations. The rate constant k_1 was calculated by the same methods as for CBr_4 , and the value varied in the same way as with CBr_4 , so only the values obtained from initial rate measurements are given in Table 3. The curves obtained with $(\text{CBrCl}_2)_2$ (0.21 mol l^{-1}) at 50 °C could not be analysed with eqns. (1) or (2). Initial rate measurements indicated zeroth-order behaviour in TMPDA .

(e) *Spin trapping.* We obtained the same spin adduct from CBr_4 in the deaerated as in the non-deaerated solutions. This showed a broad triplet with $a_N = 14.67 \text{ G}$, in accordance with previous results from this laboratory^{15c} and from studies¹⁹ of electrochemical generation of $\text{Br}_3\text{C}^\cdot$. In a recent study²⁰ of the photolytic generation of the radical, the splitting due to the proton on the α -carbon was also seen. The reason for this discrepancy is not known.

(f) *UV-Vis studies of the CT spectrum.* A solution of 0.084 M CBr_4 and 1.0 mM TMPDA in pentane showed a CT band at 380 nm with $A = 0.12$, after subtraction of the spectra of the reactants. The two components in the same

concentrations in AN showed a CT band at the same wavelength and with $A = 0.17$.

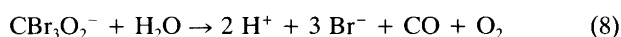
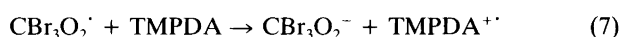
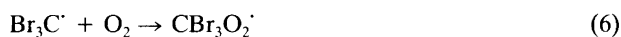
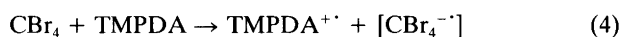
Buffered solutions. The stoichiometry of the reaction changed when tris(hydroxymethyl)aminomethane (TRIS) was added as the buffer (Table 1). Thus at least 5 mol of CBr_4 were consumed per mol of TMPDA initially present, but still each mole of consumed CBr_4 produced 4 mol of HBr . TRIS reacted with CBr_4 in the absence of TMPDA , but the reaction was far too slow to account for the changed stoichiometry. No reaction occurred in a mixture of TRIS, TMPDA and CHBr_3 . Attempts to use AcO^- or OH^- as the buffer failed because these species reacted too fast with $\text{TMPDA}^{+\cdot}$.

Discussion

The principal reason for carrying out the study presented here was to determine whether the reaction between TMPDA and CBr_4 proceeded via a rate-determining ET step and to calculate its rate constant. The previous studies with outer-sphere ET reductants (see the Introduction) afforded products and kinetic results which could be explained by an uncomplicated mechanism to give a rate law

$$\text{rate} = 2k_{\text{ET}}[\text{PHA}][\text{Red}] \quad (3)$$

according to eqn. (3). A somewhat different mechanism is suggested for the reaction with TMPDA , as outlined in Scheme 1 [eqns. (4)–(8)].



Scheme 1.

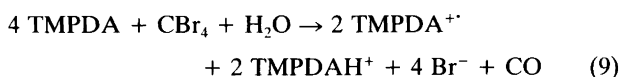
The formation of the CT complex is not included in Scheme 1 because we lack the kinetic evidence considered¹ to be necessary proof of its intermediacy. The λ_{max} (380 nm) for the CT complex between CBr_4 and TMPDA is in good accordance with the value in hexane at 77 K (400 nm).^{11a} The formation constant has been determined to be 5.3 l mol^{-1} in hexane,^{11b} and the absorbance measurements in AN and pentane indicate that the formation constant in AN should be in the same range, assuming that the extinction coefficient is constant. Thus it can be considered as a stable complex and not merely of the contact type.^{1,11b}

The obvious explanation for the formation of $\text{TMPDA}^{+\cdot}$ is an ET reaction between CBr_4 and TMPDA (see, however, below). $\text{CBr}_4^{\cdot-}$, which is formed upon ET, immedi-

ately dissociates to $\text{Br}_3\text{C}^\cdot$ and Br^- . The intermediacy of $\text{Br}_3\text{C}^\cdot$ is supported by spin-trap studies and perhaps more important, by the fact that the formation of CO was dependent on the presence of O_2 in the solution. This can be rationalized as it is known^{21,22} that $\text{Br}_3\text{C}^\cdot$ adds O_2 to form the tribromomethylperoxyl radical in a very fast reaction [eqn. (6)]. $\text{CBr}_3\text{O}_2^\cdot$ should then be further reduced [eqn. (7)], since $\text{CCl}_3\text{O}_2^\cdot$ is reduced by TMPDA²³ with a rate constant $k = 2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, and the chloro and bromo analogues are known to react equally fast as oxidants.²¹

The simultaneous (on the time scale of the experiment) formation of acid and $\text{TMPDA}^{+\cdot}$ indicates that CBr_3O_2^- is hydrolysed. Further reduction should yield not acid but OH^- and thus the stoichiometry of the reaction is best explained by eqn. (8). Carbanions of hydrocarbons with high $\text{p}K_a$ values react with O_2 to form the corresponding peroxide anion, while carbanions from hydrocarbons with $\text{p}K_a$ values of $\leq \text{ca. } 10$ do not react.²⁴ The $\text{p}K_a$ of bromoform has recently been estimated²⁵ to be 11.8 so the reverse reaction might be possible for CBr_3O_2^- . It must be stressed, however, that eqn. (8) does not represent an elementary step and should be regarded as a stoichiometric relationship. In this context it is interesting to note that CCl_3O_2^- has been shown to yield CO_2 via the formation of phosgene in pulse-radiolysis experiments in aqueous solution,²⁶ and by decomposition in CCl_4 .²⁷ This is in contrast with this study where no CO_2 was found.

From the mechanism given in Scheme 1, the rate law of eqn. (3) and the overall stoichiometry of eqn. (9) can be obtained, and it can now be seen that the yield of CO is only 40%. A partial explanation might be the formation of formic acid during the hydrolysis of dihalocarbenes.²⁸ Furthermore, the formation of neutral products and acid from



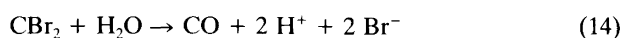
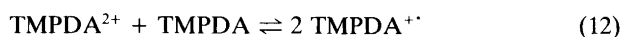
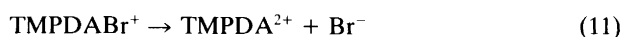
$\text{TMPDA}^{+\cdot}$ must be invoked in order to explain the yield of acid in Table 1.

The possibility of a coupling reaction between $\text{TMPDA}^{+\cdot}$ and the reactive intermediates cannot be rejected for the product runs, but the products from the reactions of $\text{TMPDA}^{+\cdot}$ will be the matter of a separate study and are not discussed here. In the kinetic runs this reaction should not be important, as shown by the high value of $[\text{TMPDA}^{+\cdot}]_{\text{max}}$. This also applies to the protonation of TMPDA, owing to the low $[\text{TMPDA}]$ used.

The disappearance of $\text{TMPDA}^{+\cdot}$ is almost zeroth order in CBr_4 and is not affected by the presence of O_2 , making it unlikely that it proceeds via oxidation to TMPDA^{2+} . This is also supported by the fact that k_2 is the same, to within experimental error, for the three perhalomethanes. The first-order rate constants at 20 and 50°C are in good but perhaps fortuitous agreement with the reported²⁹ rate constant $k = 6 \times 10^{-6} \text{ s}^{-1}$ for the disappearance of $\text{TMPDA}^{+\cdot}$ in AN at 30°C.

It has been argued that the formation of $\text{TMPDA}^{+\cdot}$ is not

evidence for an initial ET step in reductions with TMPDA,³⁰ because if the dication TMPDA^{2+} is formed, it will symproportionate with TMPDA to form two $\text{TMPDA}^{+\cdot}$ species. Thus, for the reaction with CBr_4 , an alternative to the ET mechanism is outlined in Scheme 2 [eqns. (10)–(14)]. Here an amino nitrogen on TMPDA attacks a positive bromine on CBr_4 and the intermediate



Scheme 2.

TMPDABr^+ dissociates to TMPDA^{2+} and Br^- , followed by the symproportionation reaction. Because the oxidation of TMPDA to $\text{TMPDA}^{+\cdot}$ is much slower than the symproportionation reaction ($k = 3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$),³¹ it is not possible to distinguish kinetically between the two mechanisms.³⁰ The destruction of Br_3C^- via dibromocarbene gives the same stoichiometry as in Scheme 1, so this also cannot be used in support of one of the mechanisms.

Scheme 1 is, however, favoured because the mechanism given in Scheme 2 cannot explain why O_2 is needed for the formation of CO and because the formation of $\text{TMPDA}^{+\cdot}$ is a more probable reaction than the formation of the unknown TMPDABr^+ . The mechanism of Scheme 2 serves to emphasize the possibility of substantial bonding between CBr_4 and TMPDA in the transition state, in which case the mechanism should not be considered a pure outer-sphere ET reaction.

The biphasic kinetics of CBrCl_3 and CBr_2Cl_2 indicate that they react by the same mechanism as CBr_4 , and the product studies also support this. The rate constants given in Table 3 together with the lack of reactivity of C_2Cl_6 and CHBr_3 give the following order of reactivity: $\text{CBr}_4 > \text{CBr}_2\text{Cl}_2 > \text{CBrCl}_3 \gg (\text{C}_2\text{Cl}_6 \text{ and } \text{CHBr}_3)$. The order is independent of how the rate constants are calculated, but the reactivity ratios differ slightly. The same order was previously found^{15c} for reduction by $\text{Co(II)sepalchrate}^{2+}$ and, except for C_2Cl_6 , also for $\text{CoW}_{12}\text{O}_{40}^{7-}$, although the ratio $k(\text{CBr}_4)/k(\text{CBrCl}_3)$ is only 8 for the TMPDA reaction, compared with 30 and 80, respectively, for the other reagents. This is unexpected since the reaction with TMPDA is the most endergonic of the three reactions, and therefore suggests the possibility of a bonded transition state in the TMPDA reaction.

The reaction between TMPDA and $(\text{CBrCl}_2)_2$ must follow a different mechanism. A possibility is that a reactive oxidant is formed in a rate-determining step. This can then oxidize both TMPDA to $\text{TMPDA}^{+\cdot}$ and $\text{TMPDA}^{+\cdot}$ to

TMPDA²⁺, with the symproportionation reaction [eqn. (12)] ensuring that all TMPDA²⁺ is converted into TMPDA⁺ as long as there is TMPDA present. After that, TMPDA⁺ is oxidized to TMPDA²⁺. The rate of formation and disappearance would thus be the same, and equal to the rate of formation of the oxidant, in agreement with the kinetics obtained. Further work is needed to elucidate this mechanism.

In buffered solutions at least 5 mol of CBr₄ are consumed per mol of TMPDA, once enough buffer is present (Table 1), and we therefore assume that the reaction follows another mechanism when TRIS is present. A direct reaction between TRIS and CBr₄ can, however, be excluded as shown in Table 1.

Experimental

General. All solutions were kept in the dark since both TMPDA and the halogenated alkanes are sensitive to light. In the oxygen-free runs the solutions were bubbled with Ar through high-porosity frits.

Chemicals. Carbon tetrabromide (Fluka), hexachloroethane (Fluka), 1,2-dibromotetrachloroethane (Janssen) and TMPDA (Janssen, 98%) were sublimed under vacuum. Bromotrichloromethane (Janssen) and dibromodichloromethane (Alpha Ventron) were shaken consecutively with 5 M NaOH and three portions of distilled water, and thereafter dried with 4 Å molecular sieves. CBrCl₃ was thereafter distilled, while CBr₂Cl₂ which contained 3% CBr₃Cl was used without further purification. Bromoform (Aldrich 99%+, stabilized with 1% ethanol) and PBN (Janssen) were used as received. The acetonitrile (AN) was either of Baker-analysed HPLC or Riedel Pestanal grade. Also used was AN that had been distilled twice from KMnO₄ and thereafter passed through a column of acid and neutral alumina. Doubly quartz-distilled water was used in the kinetic runs. All other chemicals were of highest commercial purity and were used as received.

Instrumentation. GLC was carried out with Varian 3300 and HP 5830 chromatographs equipped with an OV-1701 25 m×0.25 mm capillary column and an OV-101, 3% on Chromosorb W, 0.5 m column, respectively. IR spectra were recorded on a Nicolet 20 SXC-FT-IR and pH was measured with a Radiometer pH meter employing a combination glass electrode. UV-Vis spectra and kinetic measurements were recorded on a Cary 219 UV-Vis spectrophotometer, equipped with a digital interface port and connected to an HP-85 computer. Kinetic calculations were carried out either directly on the HP-85 or on an HP-9835 table-top computer using a non-linear regression program (purchased from Hewlett Packard). ESR spectra were recorded on a Bruker ER-200D SRC instrument. Ion chromatography was carried out using a suppressed IC system with a Bio-RAD IC-anion-PW column and conductimetric detection. The ions were eluted with a carbonate buffer.

Product studies. These were carried out in AN and when TRIS was present in AN-water (90:10 v/v). In a typical run 5.0 ml of a 20 mM solution of CBr₄ were mixed in a vessel with 5.0 ml of a 20 mM solution of TMPDA and the vessel was put in an oil-bath kept at 50 or 60°C. After thermal equilibration the vessel was closed with either a septum or a glass stopper. In the oxygen-free runs the solutions were deaerated with Ar (< 5 ppm, oxygen) and one of the solutions was transferred to the other by means of gas-tight syringes and septa. It was important that none of the two solutions was too concentrated because this unavoidably led to the formation of a reddish-brown precipitate upon mixing. For most of the product analysis samples of 1.0 ml were taken out for analysis after the required reaction time. When searching for trace products by GLC, work-up was also carried out on the whole reaction mixture.

GLC. The sample was mixed with 4.0 ml of 1 M HCl (saturated aqueous Na₂CO₃ was used if TMPDA and its putative products were analysed) and thereafter stirred for 1 min with 1 ml of pentane which contained the internal standard used (C₂Cl₆).

IC. The sample was mixed with 4.0 ml of water and washed with pentane. It was then further diluted to a suitable concentration with water and the carbonate buffer used for IC. A calibration curve was used for quantitation.

pH Measurements. The sample was diluted with water and if CBr₄ precipitated, a known amount of HCl was added, CBr₄ was removed with pentane and the solution was adjusted to the original pH with NaOH. Quantitation was then carried out by comparing the pH of the solution with the pH of solutions of TMPDA to which known amounts of acid had been added, or by titrating with OH⁻ to the pH of the solution before reaction.

FT-IR gas-phase analysis. The reaction mixture was acidified with 1 M HCl. A 10 ml portion of the gas phase above the solutions (20 ml) was withdrawn with a gas-tight syringe and the gas was sucked into a vacuum cell (40 ml). Quantitation was carried out by comparing the absorbance of CO in the sample with the absorbance of known [CO].

Spin trapping. A solution (0.4 ml) of CBr₄ and PBN in AN was mixed with a solution of TMPDA (0.1 ml) in AN to give a final solution which was 0.1 mol l⁻¹ in CBr₄, 2 mmol l⁻¹ in TMPDA and 0.2 mol l⁻¹ in PBN. This was allowed to stand overnight at 60°C and the residual TMPDA⁺ was quenched with 0.1 M NaOH. Both deaerated and a non-deaerated runs were carried out.

Kinetic studies. A typical kinetic run was performed as follows: 2.00 ml of a solution of CBr₄ in AN were thermostatted in the cell compartment of the spectrophotometer and thereafter 0.100 ml of a solution of TMPDA in AN

(also thermostatted if initial rates were measured) was added. The formation and disappearance of TMPDA^{++} was monitored at 611 nm, and 200 data points were automatically sampled and stored on magnetic tape. The data set was then analysed by non-linear or linear regression (see the Results). The solutions in the oxygen-free runs were deaerated and handled as previously described.^{15a}

It could be shown that k_1 at 20°C was not appreciably affected by the quality of the AN or the purification of CBr_4 and TMPDA. Control experiments also showed that the analysing light had no effect on the kinetics.

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