The Decarboxylation of Trichloroacetic Acid and the Reactions of the Trichloromethyl Anion with 1,3,5-Trinitrobenzene and with Hydrogen Ions: Kinetic Measurements in Dimethyl Sulphoxide Solution

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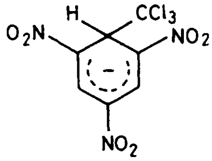
Rate measurements are reported for the formation of a Meisenheimer adduct in solutions of 1,3,5-trinitrobenzene and trichloroacetic acid or sodium trichloroacetate at very low concentrations ($<10^{-4}$M). Study of the rate constants and final absorbances of the solutions shows that the rate-limiting step is in all cases the unusually rapid unimolecular breakdown of the trichloroacetate anion (E_a 83 kJ mol^{-1}; $\Delta S^{\ddagger}$ 11 J mol^{-1} K^{-1}). The rate constants of the reactions of the trichloromethyl anion thus formed with trinitrobenzene or hydrogen ions are nearly equal. From the effect of added hydrochloric acid on the reaction rate a value of the hitherto unreported dissociation constant of trichloroacetic in DMSO (2.9 × 10^{-4} mol l^{-1}) has been deduced. Approximate deuterium isotope effects are derived for the dissociation constant and for some of the rate constants. Preliminary measurements show that the analogous breakdown of tribromoacetic acid in DMSO is a considerably faster reaction.

The decarboxylation of trichloroacetic acid has been the subject of a number of kinetic studies in several solvents.[1–5] It is generally accepted that the observed reaction is actually the decomposition of the trichloroacetate anion.[2,5] The bulk of the evidence further suggests (1) that the reaction generally requires raised temperatures and that it has an activation energy of the order of 130—170 kJ mol^{-1}, and (2) that its products are carbon dioxide and trichloromethane.[5] It is also generally accepted that the decarboxylation of the trichloroacetate ion is a unimolecular process since there is no evidence for the kinetic involvement of hydrogen ion when the reaction is carried out in aqueous acid. The argument is not entirely compelling since proton transfer from hydronium ions might make an undetectable contribution to the reaction rate in the presence of the more abundant, though weaker, proton donor water. Stronger evidence for the intermediacy of CCl_3^- in the reaction comes from the observation that addition products derived from dichloromethylene (which is known to be formed from trichloromethyl anions) can be detected when the decarboxylation is carried out in dimethoxyethane and in the presence of substrates that are reactive towards this carbene;[6] an alternative formation of dichloromethylene *via* trichloromethane is not a possibility in slightly acidic media.

In the course of a study[7] of reactions of carboxylic acids in dimethyl sulphoxide (DMSO) it was noted that solutions of trichloroacetic acid appeared to be highly unstable even at room temperature. In the presence of 1,3,5-trinitrobenzene the decomposition is accompanied by formation of the highly coloured anion (**I**), a Meisenheimer adduct of trichloromethyl anions and trinitrobenzene.[8] This observation indicates that the unstable solutions of trichloroacetic acid in DMSO are a source of trichloromethyl anions, though it does not strictly prove that these ions are actually set free.

The high rate of decomposition of trichloroacetic acid in DMSO appears to set the reaction in this solvent apart from the decarboxylation in other solvents and prompted the present investigation into its mechanism by kinetic measurements. The fact that the admixture of DMSO to aqueous solutions of trichloroacetic acid increased the rate of decarboxylation had been observed in another laboratory,[4] though the study did not extend to the anhydrous solvent. The mechanistic conclusions drawn by these investigators are unclear in that both the breakdown of the trichloroacetate ion and the protonation of trichloromethyl anions by solvated hydrogen ions are stated[4] to constitute the rate-limiting step of the reaction. We have since become aware that the troublesome instability of trichloroacetic acid in mixtures of water and DMSO had previously been noted in the course of some attempted equilibrium measurements.[9]



(I)

Besides trichloroacetic acid, the present study also includes tribromoacetic acid. Literature reports of the decarboxylation of this acid in other solvents suggest closely parallel behaviour to trichloroacetic acid, with the bromo-acid being more reactive.[5]

In previous studies of decarboxylation kinetics the progress of the reaction of trichloroacetic acid was followed either by titration of undecomposed acid or from the evolution of carbon dioxide gas. In the present work the reaction was carried out in the presence of an excess of 1,3,5-trinitrobenzene, and the observed rate was that of the increase in light absorption at 431 nm due to the formation of the ion (**I**).[8,10] This rate was found to be independent of the concentration of trinitrobenzene and must therefore correspond to a rate-limiting step that precedes the reaction of trichloromethyl anions with trinitrobenzene. The high molar absorptivity of the coloured product permitted the use of very dilute solutions ($<10^{-4}$M) of substrate.

Experimental

DMSO (Aldrich or Fisons) was fractionally distilled off calcium hydride under reduced pressure, and stored over molecular sieve (4 Å) under nitrogen. Other solvents (Fisons AnalaR) were used without purification, as was anhydrous sodium trichloroacetate (Aldrich). Trichloroacetic acid (TCAA; Aldrich) was crystallised from toluene, and traces of solvent were removed by prolonged pumping. Tribromoacetic acid (Aldrich) was crystallised from trichloromethane and dried *in vacuo* at 70 °C (P_2O_5). The dry crystals of both acids were exposed only to nitrogen before and during storage with rigorous exclusion of moisture. Stock solutions in dichloromethane were prepared in a dry box and stored for up to 4 weeks inside the dry box in flasks sealed with Parafilm. An old specimen of 1,3,5-trinitrobenzene (TNB; B.D.H.) was successively recrystallised from ethanol and trichloromethane to constant m.p. Its

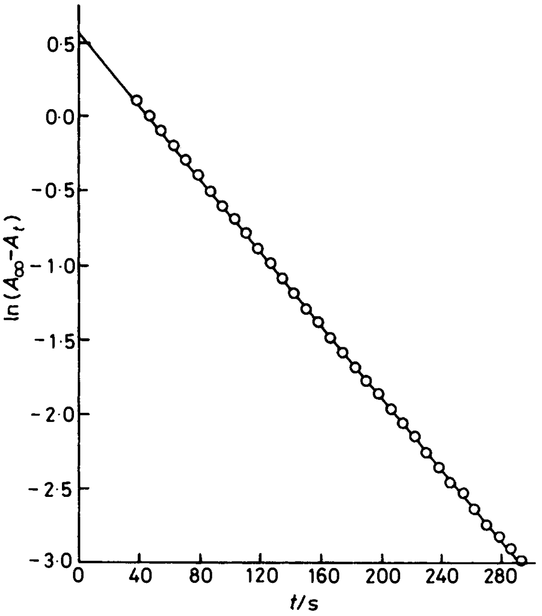


Figure 1. Illustration of first-order course of formation of (**I**) from trichloroacetic acid in DMSO

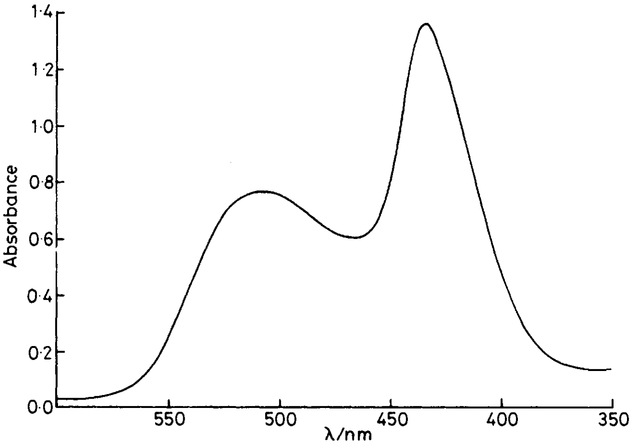


Figure 2. Spectrum of product (**I**) of decomposition of trichloroacetic acid (5.73×10^{-5}M) in the presence of 1,3,5-trinitrobenzene in DMSO

solutions in DMSO were kept in sealed vessels in the dark. Solutions developing a significant colouration were rejected. Deuterium chloride in deuterium oxide (38% w/w) was a Prochem product. Hydrochloric acid was a concentrated AnalaR solution (Fisons).

Spectrophotometric observations were made with a Pye-Unicam SP 8-100 instrument at 25.00 ± 0.05 °C (and also over a range of temperatures) with both graphical and digital recording of absorbances as a function of time.

For kinetic experiments with trichloroacetic acid, sample and reference cuvettes (1 cm path-length) were filled with 3 ml of a solution of TNB in DMSO, and allowed to reach thermal equilibrium. A small volume (5—15 μl) of a stock solution of trichloroacetic acid in dichloromethane was then injected into the sample cuvette from a Hamilton syringe, and the reactants were thoroughly mixed. The reactions were timed from the moment of injection. The change of absorbance (A) with time was monitored at the absorption maximum (431 nm) of the coloured solution produced during reaction. The first-order character of the colour-forming reaction was established from the linearity of graphs of $\ln (A_\infty - A_t)$ against time. An example is shown in Figure 1, covering progress of the reaction from *ca.* 36% (first observation) to 97%. A blank experiment established the complete absence of colour formation on addition of dichloromethane alone to the solution of TNB in DMSO.

The spectrum of the coloured solution (Figure 2) corresponds to that of a solution of the solid sodium salt of the adduct ion (**I**), prepared as previously described ($\lambda_{max.}$ 431 ± 1 and 507 ± 3 nm).[8] When tribromoacetic acid was similarly allowed to decompose in DMSO in the presence of 1,3,5-trinitrobenzene a very similar product spectrum ($\lambda_{max.}$ 433 ± 1 and 502 ± 3 nm) was obtained, consistent with the formation of the tribromo-analogue of (**I**). The ethanolic solution of the previously prepared solid sodium salt of this ion was reported to have $\lambda_{max.}$ 430 and 490 nm.[10]

The spectra of the solutions after complete reaction did not change with time (unless the solutions were exposed to daylight), indicating that the adduct (**I**) is stable under our experimental conditions.

Rate constants were normally evaluated using a computer program for first-order kinetics that did not require precise *a priori* knowledge of the value of A_∞. Graphical checks were carried out whenever major changes were made in the reaction conditions. Table 1 summarises rate constants and values of ($A_\infty - A_0$) computed for runs at different concentrations of TNB and for different initial concentrations of trichloroacetic acid.

To check on the stability of stock solutions of trichloroacetic acid in dichloromethane, such runs were repeated periodically. No significant variations in the values of k_{obs} or ($A_\infty - A_0$) were detected.

The effect of small additions of concentrated hydrochloric acid (and of the deuteriated acid) to the reaction medium was investigated in separate series of experiments (Table 2). Varying amounts of acid were added in the form of a fairly concentrated solution in water or in deuterium oxide, the total volume of the addition being kept at the constant value of 5 μl (for 3 ml of reaction solution). The addition of concentrated acids was made from an all-plastic Finnpipette with an accuracy of *ca.* ±5% in the measured volume.

Results for the effect of varying additions of dichloromethane and dioxane and of water and deuterium oxide to the reaction media are given in Tables 3 and 4, respectively. They serve to establish that the addition of co-solvents in low concentration, as in our procedure of making up reaction mixtures, does not seem to have a significant effect on the measurements. Rates of decomposition of sodium trichloroacetate (NaTCA) were obtained by analogous procedures (Table 5). The stock solution of the substrate was in this case made up in water and in all these experiments the total volume of added water was kept at the same value (4 μl for a volume of 3 ml of reaction solution). Rate measurements over a range of temperatures are reported in Table 6. An Arrhenius plot of these results (Figure 3) leads to an activation energy of 83 ± 2 kJ mol^{-1}.

Discussion

The first-order rate constant of the colour-forming reaction [the formation of the adduct ion (**I**)] shows no significant change as the concentration of TNB is varied over a two-fold range (Table 1). Accordingly, the rate-limiting step does not involve participation by TNB and the reaction observed is an uncatalysed decarboxylation. The decarboxylation must be the unimolecular reaction of the trichloroacetate ion and not that of trichloroacetic acid (or a kinetically equivalent bimolecular reaction between isolated hydrogen ions and trichloroacetate

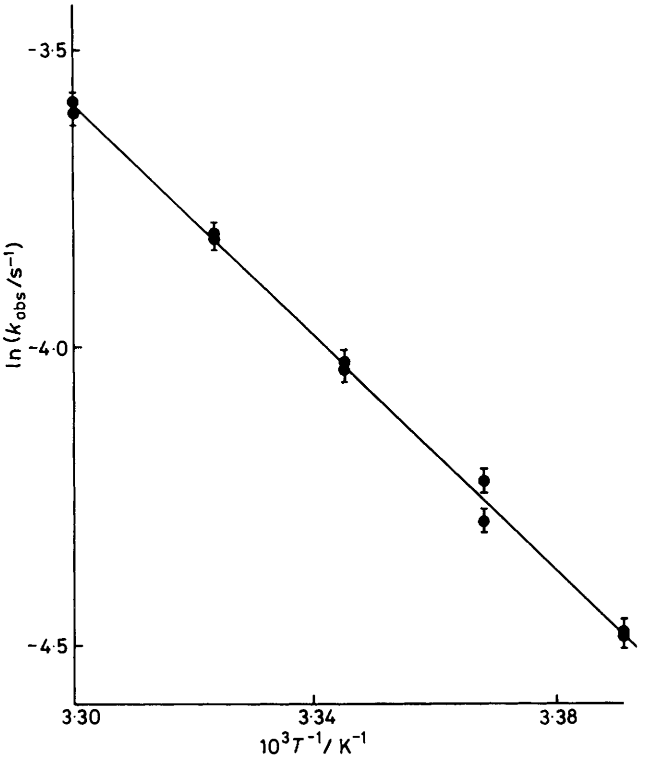


Figure 3. Arrhenius plot for decomposition of sodium trichloroacetate in DMSO

ions). This conclusion follows from the observations (i) that the rate is dramatically depressed by addition of hydrochloric acid (Table 2), which would reduce the fraction of the substrate present as the anion, (ii) that the rate constant shows a slight decrease as the concentration of substrate is increased, consistent with incomplete dissociation of trichloroacetic acid at the higher concentrations (Table 1), and (iii) by the close correspondence of the observed rate constant for the decarboxylation of sodium trichloroacetate with that for trichloroacetic acid at the lowest concentrations, implying that at those concentrations trichloroacetic acid is almost completely dissociated.

The complete reaction scheme for the formation of (**I**) is accordingly written as (1)—(3). The rate constant k_3 of the

$$CCl_3CO_2H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CCl_3CO_2^- + H^+_{solv} \quad \text{rapid} \qquad (1)$$

$$CCl_3CO_2^- \xrightarrow{k_2} CCl_3^- + CO_2 \quad \text{rate-limiting} \qquad (2)$$

$$CCl_3^- + TNB \xrightarrow{k_3} (I) \qquad (3)$$

scavenging process (3) is large, so that this step does not affect the overall rate of reaction. For the experiments with sodium trichloroacetate (Table 5) the value of the observed rate constant should be equal to k_2.

According to this scheme the observed rate constant for trichloroacetic acid should be proportional to the ratio $[CCl_3CO_2^-]/[TCAA]_{st}$ (where $[TCAA]_{st}$ is the overall or stoicheiometric concentration of the acid), and the addition of hydrogen ions to the solution should depress this rate by a mass-law (or common-ion) effect, expressible in terms of the equation dissociation constant K_{HA} of trichloroacetic acid as

$$\frac{[CCl_3CO_2^-]}{[CCl_3CO_2H]} = \frac{K_{HA}}{[H^+_{solv}]} \qquad (4)$$

(4). Since the sum of the actual concentrations of trichloroacetic acid and trichloroacetate ions is equal to $[TCAA]_{st}$ equation (5)

$$\frac{[CCl_3CO_2^-]}{[TCAA]_{st}} = \frac{K_{HA}}{[H^+_{solv}] + K_{HA}} \qquad (5)$$

follows. Provided $[H^+_{solv}] \gg [CCl_3CO_2^-]$, the observed rate may be written either in terms of the overall concentration or in terms of the trichloroacetate concentration [equations (6) and

$$d[(I)]/dt = k_{obs}[TCAA]_{st} \qquad (6)$$

$$= k_2[CCl_3CO_2^-] \qquad (7)$$

(7)]. Combination of equations (5)—(7) results in (8), which can be rearranged as (9). Equation (9) is in a convenient form for

$$k_{obs} = k_2K_{HA}/([H^+_{solv}] + K_{HA}) \qquad (8)$$

$$k_{obs}^{-1} = k_2^{-1} + [H^+_{solv}]/k_2K_{HA} \qquad (9)$$

graphical evaluation of the constants from a linear plot of k_{obs}^{-1} *versus* $[H^+_{solv}]$.

This analysis can be tested by the results of experiments on the effect of added hydrochloric acid (Table 2). In these experiments the concentration of hydrochloric acid always greatly exceeded [TCAA] so that, to a good approximation, the substrate acid makes a negligible contribution to the concentration of hydrogen ions in solution. Hydrochloric acid is also a stronger acid, but it may nevertheless not be assumed to be fully dissociated. Its dissociation constant in anhydrous DMSO has been measured[11] as 0.01 mol l^{-1} and we have taken this value also to apply to DMSO solutions containing 0.09M-water. The values of $[H^+_{solv}]$ calculated in this manner are slightly smaller than the stoicheiometric concentrations over the range of concentrations used in the experiments. They have been used for the graphical test of equation (9) reproduced in Figure 4. Except for the anomalous points at the highest concentrations [and the point corresponding to the experiment without addition of hydrochloric acid, for which equation (9) does not hold], the predicted linear relation is confirmed. The slope of this graph gives $k_2K_{HA} = 4.2 \times 10^{-6}$ mol l^{-1} s^{-1}. On combining this value with the result for k_2 (1.45×10^{-2} s^{-1}, the average for the experiments on the decomposition of sodium trichloroacetate; Table 5), we obtain the value of the dissociation constant of trichloroacetic acid in DMSO (containing 0.09M-water) as 2.9×10^{-4} mol l^{-1}. This result represents the first determination of the dissociation constant, earlier attempts at direct measurement having been frustrated by the instability of the solutions.[9b] Since the difference between the calculated concentration of hydrogen ions and the stoicheiometric concentration of hydrochloric acid is small, the result is not very sensitive to the precise value of K_{HCl}. The intercept of the graph in Figure 4 is small and does not directly lead to a reliable value of k_2, but it is compatible with the value obtained from the decomposition of sodium trichloroacetate (which is marked on the vertical axis by a triangle).

The rate constants obtained in experiments with added deuterium chloride (Table 2) can be analysed by the same procedure. The calculation of the precise concentration of D^+_{solv} ions requires an assumption concerning the dissociation constant of DCl in DMSO solution. The graph to fit equation (9) was therefore constructed on the basis of two extreme assumptions: (a) that K_D has the same value as K_H, and (b) that

Table 1. Results for decomposition of trichloroacetic acid at varying initial concentrations of substrate and of trinitrobenzene at 25 °C

$10^5[\mathrm{TCAA}]_0/\mathrm{M}$	$10^3[\mathrm{TNB}]/\mathrm{M}$	$10^4 k_{\mathrm{obs}}/\mathrm{s}^{-1}$	$(A_\infty - A_0)$	$10^{-3}(A_\infty - A_0)/[\mathrm{TCAA}]_0$
7.42	4.6	118	1.923	25.9
7.42	5.3	115	1.937	26.6
7.42	6.0	124	1.889	25.5
7.42	6.6	121	1.904	25.7
7.42	8.3	123	1.922	25.9
7.42	10.0	114	2.021	27.2
2.85	10.0	147	0.827	29.0
3.42	10.0	142	0.936	27.4
3.99	10.0	145	1.112	27.9
4.56	10.0	137	1.324	29.0
5.13	10.0	140	1.391	27.1
5.70	10.0	135	1.580	27.7
6.28*	10.0	125	1.766	28.1
6.85	10.0	132	1.869	27.3
7.42	10.0	114	1.915	25.8
7.99	10.0	120	2.165	27.1

* Experimental points for this run are plotted in Figure 1.

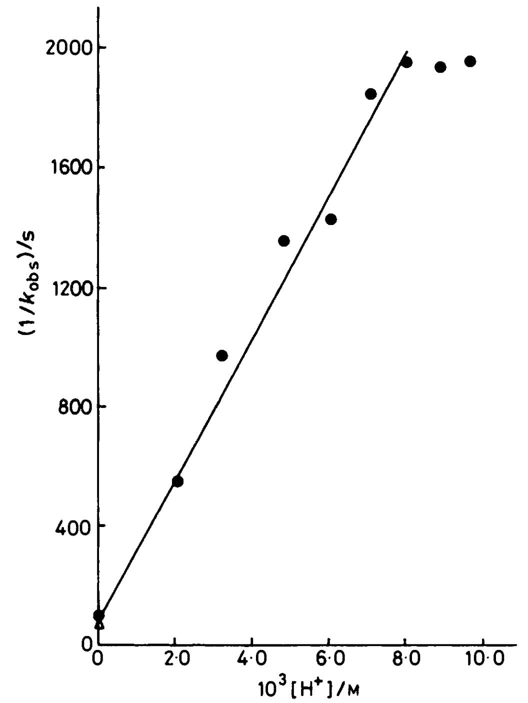


Figure 4. Test of equation (9): graphical evaluation of dissociation constant of trichloroacetic acid in DMSO

$K_{\mathrm{DCl}}/K_{\mathrm{HCl}} = 4$. The desired values of $K_{\mathrm{CCl_3CO_2D}}$ are then 2.6×10^{-4} or 1.7×10^{-4} mol l^{1}, respectively. The ratio $K_{\mathrm{CCl_3CO_2H}}/K_{\mathrm{CCl_3CO_2D}}$ is accordingly within the range 1.1—1.7. These values of the isotope effect would hardly be affected if a slightly different value were chosen for K_{HCl} [subject to the same assumptions (a) and (b) concerning K_{DCl}]. It may also be noted that, on any sensible view of the decarboxylation of the carboxylate ion, the rate constant k_2, required in the evaluation of $K_{\mathrm{CCl_3CO_2D}}$, is not subject to a deuterium isotope effect. The calculated isotope effect on the dissociation constant of trichloroacetic acid is therefore not subject to uncertainties from this source.

For the experiments in which trichloroacetic acid is the only solute, the gradual decrease of the observed rate constants at increasing concentrations of trichloroacetic acid may qualitatively be interpreted as being due to changes in the degree of dissociation of the acid. The effect is approximately of the order of magnitude required by the dissociation constant. We have not attempted to elaborate the analysis of this quite small rate decrease because the total concentration of trichloroacetic acid decreases throughout a run (so that the reaction should, in principle, not be strictly first-order), forming at the same time the acid consisting of (**I**) and the solvated hydrogen ion as the counter-ion. This (nitronic ?) acid is expected to be very strong, but the value of its dissociation constant is unknown. As will now be discussed, the reaction also yields some trichloromethane, which is not measurably acidic in these solutions. This side reaction would further complicate a quantitative theory.

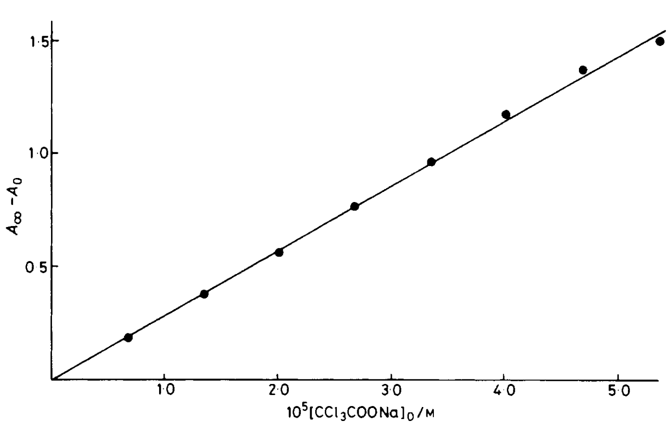


Figure 5. Absorbance change for complete decomposition of sodium trichloroacetate in the presence of 1,3,5-trinitrobenzene, as a function of concentration of sodium trichloroacetate

The final absorption spectra of the reaction mixtures show two maxima (the higher one at 431 nm and a lower, much broader one at *ca.* 507 nm) which correspond closely to the absorptions reported[10] for the sodium salt of (**I**) in ethanol (at 427 and 495 nm) and are identical with those observed in the present study for solutions of this salt in DMSO. The difference between final and initial absorbances ($A_\infty - A_0$) at 431 nm of solutions of the sodium salt of (**I**), present after complete decomposition of sodium trichloroacetate in kinetic runs (Table 5), was accurately proportional to the initial concentration of sodium trichloroacetate (Figure 5). On the assumption that

Table 2. Results for decomposition of trichloroacetic acid at 25 °C in the presence of added HCl and DCl at different concentrations. $[H_2O]$ or $[D_2O]$ 0.09M, $[TCAA]_0$ 7.41 × 10^{-5}M, [TNB] 9.9 × 10^{-3}M

10^3[HCl]/M	$10^3[H^+_{solv}]$*/M		$10^5k_{obs}/s^{-1}$	$(A_\infty - A_0)$	$10^3(A_\infty - A_0)/[TCAA]_0$
0.0	0.0		1 046	1.876	25.3
2.4	2.0		181	1.524	20.6
4.7	3.5		102	1.269	17.1
7.1	4.8		73	1.145	15.5
9.5	6.0		70	1.007	13.6
11.8	7.0		54	0.847	11.4
14.2	7.9		51	0.802	10.8
16.6	8.8		51	0.828	11.2
18.9	9.6		51	0.806	10.9
10^3[DCl]/M	$10^3[D^+_{solv}]$/M				
0.0	*a**	*b*†	1 100	1.842	24.9
2.2	1.9	1.4	146	1.460	19.7
4.5	3.4	2.3	113	1.368	18.5
6.7	4.6	3.0	72	1.097	14.8
8.9	5.7	3.6	62	1.000	13.5
11.1	6.7	4.2	51	0.872	11.8
13.4	7.6	4.7	48	0.745	10.1
15.6	8.5	5.1	47	0.772	10.4
17.8	9.2	5.5	44	0.707	9.5

* Calculated for K_{HCl} (K_{DCl}) 0.01. † Calculated for K_{DCl} 0.0025.

Table 3. Results for decomposition of trichloroacetic acid at 25 °C in the presence of dichloromethane and dioxane at different concentrations. $[TCAA]_0$ 6.85 × 10^{-5}M, [TNB] 8.3 × 10^{-3}M

	$[CH_2Cl_2]$/M	$10^4k_{obs}/s^{-1}$	$(A_\infty - A_0)$
(a)	0.06*	135	1.681
	0.58	111	1.795
	1.10	97	1.860
	1.62	82	1.772
	2.14	81	1.809
	2.65	68	1.764
(b)	[Dioxane]/M†	$10^4k_{obs}/s^{-1}$	$(A_\infty - A_0)$
	0.00	135	1.681
	0.39	136	1.752
	0.78	121	1.819
	1.17	124	1.808
	1.56	116	1.833
	1.95	106	1.827

* Concentration due to addition of stock solution of trichloroacetic acid.
† 0.06M-Dichloromethane additionally present.

Table 4. Results for decomposition of trichloroacetic acid at 25 °C in the presence of added water and deuterium oxide. $[TCAA]_0$ 7.18 × 10^{-5}M, [TNB] 9.6 × 10^{-3}M

$[H_2O]$/M	$10^4k_{obs}/s^{-1}$	$(A_\infty - A_0)$	$(A_\infty - A_0)/[TCAA]_0$
0.000	105	1.695	23.6
0.357	86	1.682	23.4
0.713	76	1.554	21.6
1.070	75	1.224	17.0
1.427	66	0.776	10.8
1.783	61	0.514	7.2
$[D_2O]$/M			
0.000	107	1.712	23.8
0.355	84	1.705	23.7
0.709	90	1.599	22.3
1.063	76	1.437	20.0
1.418	68	1.099	15.3
1.772	63	0.772	10.8

this absorbance difference is due entirely to (**I**), the molar absorption coefficient (ε) of (**I**) at 431 nm is calculated as (2.89 ± 0.05) × 10^4 and, correspondingly, that at *ca.* 507 nm as 1.63 × 10^4 $\text{mol}^{-1}\ \text{l}\ \text{cm}^{-1}$. The spectrum may be compared with the spectra of alkoxide Meisenheimer adducts of picryl ethers for which the absorption maxima in various solvents are typically *ca.* 415 nm (ε *ca.* 2.8 × 10^4) and 500 nm (ε *ca.* 1.9 × 10^4 $\text{mol}^{-1}\ \text{l}\ \text{cm}^{-1}$).[12]

The apparent molar absorption coefficients of the product in the reactions with trichloroacetic acid show a slight decrease as the initial concentration of trichloroacetic acid is raised, and there is a much more pronounced drop as increasing amounts of hydrochloric acid are added to the reaction mixtures (see final columns of Tables 1 and 2). At low initial concentrations of substrate without added acid the molar absorption coefficient of product is approximately the same as in the experiments with sodium trichloroacetate, which suggests that for both reactions the light-absorbing product is the adduct ion (**I**) (see Figure 2). One possible explanation of the decrease in molar absorption coefficient in more acidic solutions is the reversible or irreversible conversion of that ion into a different chemical species with a lower molar absorption coefficient at 431 nm. Irreversible destruction of the product ion is, however, ruled out by the observation that in all solutions, provided they are protected from daylight, infinity readings did not change during a time interval of several reaction half-lives. The reversible formation of a less absorbing product, *e.g.* by conversion of (**I**) into an un-ionised nitronic acid,[13] can also be discounted on the basis of the following set of experiments. The reaction was allowed to proceed to completion in two cells containing identical initial concentrations of trichloroacetic acid and trinitrobenzene acid producing solutions of identical final absorbance. Successive amounts of concentrated hydrochloric acid (up to a total amount of 10 μl, corresponding to a concentration of 0.04M) were then added to only one of the cells, but both cells were otherwise treated in an identical manner. The absorbances of the cells were compared after each addition, and found to fall very slightly during their exposure to daylight (by *ca.* 0.035). However, there was no significant difference

Table 5. Results for decomposition of sodium trichloroacetate at varying initial concentrations at 25 °C. $[H_2O]$ 0.072M, [TNB] 0.0100M

$10^5[NaTCA]_0$/M	$10^4k_{obs}/s^{-1}$	$(A_\infty - A_0)$
0.67	132	0.188
1.33	139	0.382
2.00	144	0.565
2.66	134	0.770
3.33	161	0.964
4.00	160	1.169
4.66	156	1.365
5.33	138	1.498
	Average 145 ± 12 (s.d.)	

between the absorbances of the two solutions. Accordingly, the diminished final absorbance observed for reaction media containing up to 0.019M-hydrochloric acid (Table 2) cannot be due to reversible or irreversible reaction of the coloured product with acid.

It is thus concluded that the acid interferes with the formation of the product. Since the effect of low concentrations of added acid on the observed reaction rate is entirely explained by the depression of the dissociation of trichloroacetic acid, this interference must occur through competition at a product-forming step subsequent to the rate-limiting process, through competition with reaction (3). We have detected the formation of trichloromethane in the n.m.r. spectra of decomposed solutions of trichloroacetic acid in DMSO. Although we could not directly monitor the formation of this product at the very low concentrations of our kinetic experiments, it seems reasonable to conclude that reaction (10) is in competition with

$$CCl_3^- + H^+_{solv} \xrightarrow{k_4} CHCl_3 \qquad (10)$$

reaction (3). Equations (11)—(15) follow from this model. A graphical test of equation (15) is shown in Figure 6. The straight

$$\frac{[(I)]}{[CHCl_3]} = \frac{k_3[TNB]}{k_4[H^+_{solv}]} \qquad (11)$$

$$[TCAA]_0 = [(I)]_\infty + [CHCl_3]_\infty \qquad (12)$$

$$= [(I)]_\infty \left\{1 + \frac{k_4[H^+_{solv}]}{k_3[TNB]}\right\} \qquad (13)$$

$$= \frac{(A_\infty - A_0)}{\varepsilon_{431}} \left\{1 + \frac{k_4[H^+_{solv}]}{k_3[TNB]}\right\} \qquad (14)$$

$$\frac{[TCCA]_0}{(A_\infty - A_0)} = \frac{1}{\varepsilon_{431}} + \left\{\frac{k_4}{\varepsilon_{431}k_3[TNB]}\right\}[H^+_{solv}] \qquad (15)$$

line drawn cuts the vertical axis with an intercept corresponding to the previously measured molar absorption coefficient. From the slope of the line the ratio k_4/k_3 is evaluated as 1.7.

In aqueous solution the reaction between trichloromethyl anions and solvated hydrogen ions is thought to proceed at an essentially encounter-controlled rate.[14] If the same were true for this reaction in DMSO solution, then the closeness of the values of k_3 and k_4 would imply that the capture of trichloromethyl anions by TNB is also a virtually encounter-controlled process. However, in the light of other competitive studies,[15] it seems that these reactions may proceed more slowly, perhaps because desolvation of the hydrogen ion from DMSO (which accompanies the proton transfer) contributes to the energy barrier.

Table 6. Results for decomposition of sodium trichloroacetate at different temperatures. $[H_2O]$ 0.072M, $[NaTCA]_0$ 5.33×10^{-5}M, [TNB] 0.0100M

T/K	$10^4k_{obs}/s^{-1}$
295.2	113
295.2	110
297.2	145
297.2	136
299.2	176
299.2	177
301.2	219
301.2	219
303.2	269
303.2	275

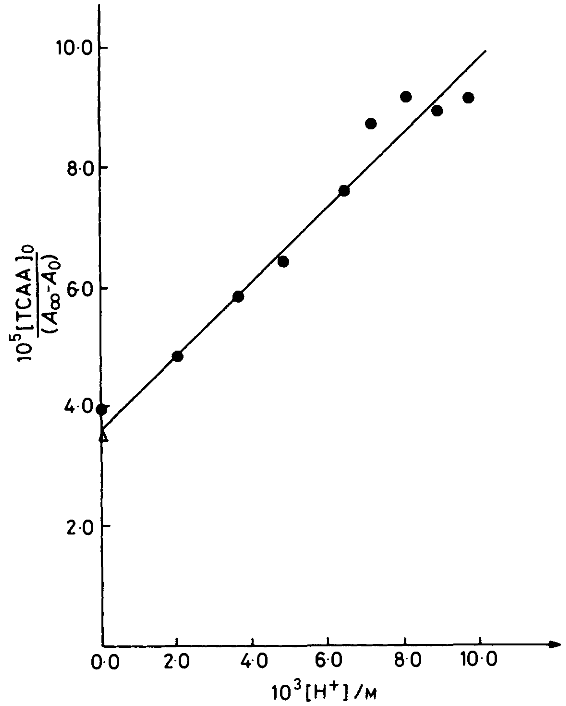


Figure 6. Test of equation (15), illustrating competition between hydrogen ions and 1,3,5-trinitrobenzene for trichloromethyl anions

The above calculation assumes that only the solvated hydrogen ion is involved in the trichloromethane-forming reaction, as in equation (10), *i.e.* the possibility of reaction (16) is ignored. It could alternatively be supposed that HCl is also effective. Since, irrespective of minor uncertainties, reaction (10) must be very fast, it follows that the rate constant k_5 for proton transfer (16) from HCl cannot be substantially larger than k_4

$$CCl_3^- + HCl \xrightarrow{k_5} CHCl_3 + Cl^- \qquad (16)$$

(which refers to a nearly encounter-controlled process). We may therefore suppose that an alternative extreme value of k_4/k_3 may be calculated by use of the assumption $k_5 = k_4$ (which is mathematically equivalent to the simpler calculation of k_4 with $[H^+_{solv}] = [HCl]_{st}$). This value of the ratio k_4/k_3 (evaluated as k_5/k_3) is 1.15.

The final absorbance values for the reaction in the presence of deuterium chloride (instead of ordinary hydrogen chloride) can be treated in the same way [and again with the assumptions (a) $K_{DCl} = K_{HCl}$ and (b) $K_{HCl}/K_{DCl} = 4$]. From the slope of the graphs of equation (15), we thus find a value of between 2.1 and 3.6 for the ratio $k_4{}^D/k_3$. The kinetic isotope effect (k^H/k^D) for the

$$CCl_3{}^- + D^+{}_{solv} \xrightarrow{k_4{}^D} CDCl_3 \qquad (17)$$

reaction of trichloromethyl anions with solvated H^+ or D^+ ions, given by $k_4/k_4{}^D$, accordingly lies in the range 0.8—0.5, implying a small but unexpectedly inverse isotope effect. Again, the calculation can also be carried out with the assumption $k_5 = k_4$, leading to a more expected value $k_4/k_4{}^D = 1.1$ for the kinetic isotope effect.

The high rate of decomposition of the trichloroacetate ion in DMSO, compared with other solvents,[5] is associated with an Arrhenius energy of activation of 83 ± 2 kJ mol^{-1} (19.8 ± 0.5 kcal mol^{-1}) and a very small positive entropy of activation of 11.5 ± 2 J K^{-1} mol^{-1} (2.8 ± 0.5 cal K^{-1} mol^{-1}) as deduced from an Arrhenius plot (Figure 3) of the data in Table 6. The entropy value suggests that solvation changes in the formation of the transition of state from the trichloroacetate ion must be minimal. This is in accordance with the more general experience that DMSO is not very effective in stabilizing anions by solvation, so that differences in solvation between different anions must be small. It is this relatively feeble solvation which also accounts for the instability of the trichloroacetate ion in DMSO.

The considerations concerning solvation should apply with equal or greater force to the tribromoacetate ion. This expectation is fully borne out by the even higher reactivity of tribromoacetic acid in DMSO solvation. At concentrations of 6.6×10^{-5}M (at which, by analogy with trichloroacetic acid, the acid whould be largely dissociated), the rate of decomposition was too great for the determination of rate constants by conventional spectrophotometry. Addition of hydrochloric acid (0.04M) reduced the value of the first-order rate constant at 25 °C to 0.02 s^{-1}, from which we conclude that the decomposition of the tribromoacetate ion is probably between 10 and 100 times more rapid than that of the trichloroacetate ion.

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