Decomposition of Hexachloroacetone in Dimethyl Sulphoxide Solution: a Source of Trichloromethanide Anions

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Hexachloroacetone (HCA) decomposes in dimethyl sulphoxide solution at room temperature. In the presence of an excess of 1,3,5-trinitrobenzene (TNB) the progress of the reaction can be monitored by the appearance of the visible absorption characteristic of the formation of the trichloromethyl Meisenheimer adduct of TNB in nearly quantitative yield (2 mol of adduct per mol of HCA). The reaction is slower than the decomposition of trichloroacetic acid under the same conditions, the difference being attributable to a large negative entropy of activation. The reaction rate is markedly increased by the addition of water and slightly depressed by addition of acid. The kinetics are consistent with a rate-limiting breakdown of the *gem*-diol hydrate of HCA into trichloroacetic acid and trichloromethanide anions, followed by the more rapid decomposition of trichloroacetic acid.

There have been a number of reports of the breakdown of hexachloroacetone (HCA) in the presence of bases or nucleophiles as providing synthetically useful reactions. With hydroxide ions in aqueous solution HCA is stated to undergo a typical haloform reaction (1) according to the second-order rate law

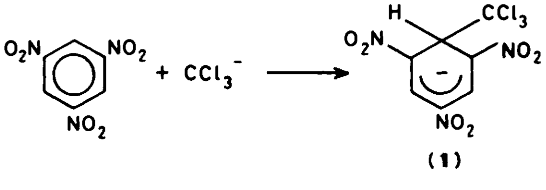
$$(CCl_3)_2CO + OH^- \longrightarrow CCl_3CO_2^- + CHCl_3 \quad (1)$$

implied by the equation.[1] The reaction is the basis of patented procedures for the production of trichloromethane.[2] In such reactions it is expected that chloroform is formed by proton transfer from water to the intermediate trichloromethanide anion. The formation of trichloroacetic acid (TCAA) may be viewed as the trichloroacetylation of water. Other nucleophiles, especially primary and secondary amines,[3–5] dipeptides,[6] and alcohols[7,8] can similarly be trichloroacetylated by HCA. Dimethyl sulphoxide (DMSO) and similar solvents have advantages in that they allow such reactions to be carried out in the absence of added base.[6,8,9] On the other hand, the reaction of alkoxide with HCA in non-hydrogen-bonding solvents, such as light petroleum, leads to products derived from the breakdown of trichloromethanide anions into the carbene and chloride ions,[10,11] and the use of HCA as a source of positive halogen has also been reported.[12]

We have recently reported that the use of DMSO allows the isolation of products derived from trichloromethanide anions. The anions are formed when TCAA decomposes in DMSO at room temperature[13,14] or when tetrachloromethane or bromotrichloromethane reacts with tin(II) halides.[15] In either case, trichloromethanide anions can be trapped by virtue of their reactions with aromatic aldehydes[14,16] [reaction (2)] or with

$$ArCHO + CCl_3^- \longrightarrow ArCH(CCl_3)O^- \xrightarrow{(+H^+)} ArCH(CCl_3)OH \quad (2)$$

1,3,5-trinitrobenzene (TNB)[13,17] [reaction (3)]. The decomposition of TCAA has been shown to give a quantitative yield of the Meisenheimer adduct ion which is the product of reaction (3).[17]



(1)

(3)

It seemed of interest to examine the decomposition of HCA in the context of these earlier studies. The reported formation of TCAA as one of the products requires the involvement of water at some stage, and we have sought to establish the nature of this intervention. A further point of interest concerns the fate of the product trichloroacetic acid. According to our earlier studies, this substance is not stable in DMSO solution,[13,17] and the role of its decomposition as part of the general reaction scheme for HCA had to be established.

Experimental

Dimethyl sulphoxide (DMSO) (Aldrich) was dried for several days over molecular sieve (4 Å), distilled under reduced pressure from calcium hydride, and kept out of contact with the atmosphere. The water content of pure DMSO and of solutions containing added water was monitored by the coulometric Karl Fischer method using a Mitsubishi Moisture Meter. Dichloromethane (Fisons AnalaR) and hexachloroacetone (98%+; Aldrich) were used without purification.

The preparation of 1,3,5-trinitrobenzene (TNB) from picryl chloride (1-chloro-2,4,6-trinitrobenzene) by reaction with sodium iodide and acetic acid was attempted, following the procedure described by Blatt and Tristram.[18] However, we found the predominant product to be 1-iodo-2,4,6-trinitrobenzene. Our observation is confirmed in a paper by Blatt and Gross[19] who later reported the same method as a route to picryl iodide. Our preparations subsequently used the formation of pure picryl iodide as the first stage. This intermediate is readily purified by crystallization from benzene. Hydriodic acid is added to its solution in acetone and the solution is poured into an aqueous solution of sodium hydrogen sulphite. The precipitated TNB was successively recrystallized from ethanol and from tetrachloromethane to yield a virtually colourless product. Purification of samples prepared by this method proved easier than that of material from other sources.

Product of Reaction between HCA and TNB in DMSO.—Injection of a dilute solution of HCA (7 μl; 0.0095M) in dichloromethane into a solution of TNB in undried DMSO (3 ml; 0.01M) slowly produced a solution with a u.v.–visible absorption spectrum identical in shape with that previously reported[17] for the Meisenheimer adduct ion (**1**). The absorbance at the main maximum (431 nm) indicated a concentration of 3.7×10^{-5}M for (**1**) (as compared with an initial concentration of HCA in the mixture of 2.2×10^{-5}M). The result

Table 1. Effect of TNB concentration at 25 °C

$[HCA]_0 = 3.335 \times 10^{-5}$M

10^2[TNB]/M	[TNB]/[HCA]	$10^3[H_2O]$/M	$10^4k_{obs}/s^{-1}$	$(A_\infty - A_0)$	2φ
0.341	102	4.8 ± 1.5	11.6	1.65	1.71
0.682	204	4.4 ± 1.2	11.6	1.79	1.86
1.364	407	4.5 ± 1.3	11.2	1.48	1.54
2.046	611	4.4 ± 1.2	11.1	1.74	1.81

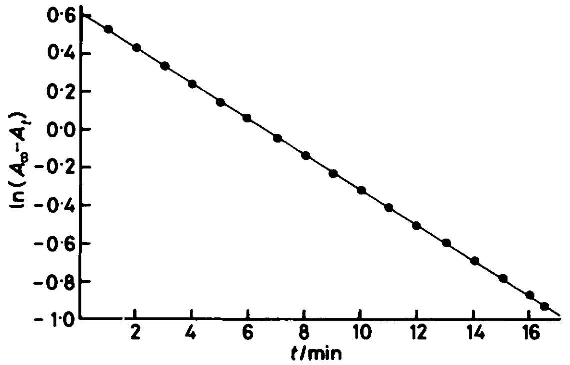


Figure 1. Illustration of first-order rate law ($[HCA]_0 = 3.5 \times 10^{-5}$M; $[TNB]_0 = 0.035$M)

Table 2. Effect of water concentration at 25 °C

$[HCA]_0 = 3.335 \times 10^{-5}$M; [TNB] = 0.02M

$[H_2O]$/M	$10^4k_{obs}/s^{-1}$	$(A_\infty - A_0)$	2φ
0.0030	9.7	1.856	1.93
0.0035	8.0	1.780	1.85
0.0037	9.6	1.778	1.84
0.0049	10.6	1.730	1.79
0.0124	15.3	1.701	1.76
0.0160	13.8	1.730	1.79
0.0276	14.7	1.780	1.85
0.0282	14.0	1.781	1.85
0.0550	17.0	1.782	1.85
0.0755	18.9	1.710	1.77
0.1495	19.4	1.712	1.78
0.463	23.6	1.663	1.73
0.923	22.7	1.552	1.61
0.929	25.5	1.530	1.59
1.389	31.1	1.113	1.15
1.852	31.9	0.765	0.79
1.852	35.1	0.696	0.72
2.96	75	0.227	0.24
3.70	108	0.153	0.16

implies the formation of 1.7 mol of (**1**) per mol of HCA, the shortfall from the expected ratio (2:1) probably being accounted for by reaction (4). This inference is further examined later.

$$CCl_3^- + H_2O \longrightarrow CHCl_3 + OH^- \qquad (4)$$

A solution containing equal concentrations (0.75M) of both HCA and TNB in $[^2H_6]$DMSO containing added water (0.11M) gave the proton n.m.r. spectrum previously reported for (**1**) (but containing an additional peak at δ 7.7 possibly attributable to residual hexachloroacetone hydrate). Only with added water did the solution exhibit the intense colour characteristic of the Meisenheimer adduct (**1**). The observation suggests that breakdown of HCA is either very slow or impossible in the absence of water.

Kinetic Measurement.—Samples were prepared as described for the preceding measurement of the absorption spectrum of the Meisenheimer adduct, with typical initial concentrations of TNB and HCA of 0.02 and 3.3×10^{-5}M, respectively. Absorbance measurements at 431 nm were recorded with a Pye-Unicam SP8-100 spectrophotometer at fixed time intervals from the time of mixing. Cells of 1 cm path length were maintained thermostatically at 25 °C unless specified otherwise. The reference cell contained an identical solution of TNB (without the addition of the HCA solution in dichloromethane). Stock solutions of TNB were freshly prepared and protected from light. Once the importance of trace concentrations of water was appreciated, all glassware was scrupulously dried and solutions were mixed by syringe transfer between septum-sealed vessels under positive pressure.

The rate of formation of (**1**) is monitored by this procedure, and the fraction of undecomposed HCA can be deduced. On the basis of earlier work[17] we concluded that the Meisenheimer adduct is formed in a rapid process from CCl_3^- anions, the formation of which is rate-limiting.

Let us assume that a fraction φ of the CCl_3^- anions formed is converted into (**1**). Provided φ stays sensibly constant during any one run, the relations (5) and (6) will hold for the absorbances A_t, A_0, A_∞ of the solution at a wavelength at which (**1**) is the main absorbing species with molar absorption coefficient ε_1, at times *t*, zero, and infinity. If the reaction is of first order with respect to HCA and goes to completion, equation (7) and hence equation (8) will apply.

$$(A_\infty - A_0) = 2\varphi[HCA]_0\,\varepsilon_1 \qquad (5)$$

$$(A_\infty - A_t) = 2\varphi[HCA]_t\,\varepsilon_1 \qquad (6)$$

$$[HCA]_t = [HCA]_0 \exp(-kt) \qquad (7)$$

$$\ln[(A_\infty - A_0)/(A_\infty - A_t)] = kt \qquad (8)$$

The experimental results are fully compatible with these assumptions. The run in Figure 1, covering *ca.* 80% of the reaction, illustrates the first-order character of the kinetic process and the degree of reliability of the extrapolated value of $(A_\infty - A_0)$. In general, the rate constant and $(A_\infty - A_0)$ were obtained by an interactive computer program; there was no systematic difference between computed and graphically evaluated results. Table 1 gives the results for one set of runs in which the concentration of TNB changes by a factor of six, while the concentration of water is kept constant and low. The results (and several additional similar sets) show a relatively slight decrease in rate constant as the concentration of TNB is increased. For the same runs the values of $(A_\infty - A_0)$ are reasonably constant with a random scatter. The final column

Table 3. Effect of added acid at 25 °C

$[\mathrm{HCA}]_0 = 3.335 \times 10^{-5}$M; [TNB] = 0.02M

(Vol. aq. HCl added to 3 ml)/µl	10^3[HCl]/M	$[\mathrm{H_2O}]_{\mathrm{added}}$/M	$10^4k_{\mathrm{obs}}/\mathrm{s}^{-1}$	$(A_\infty - A_0)$	2φ
0	0	0	9.3	1.708	1.77
1	3.8	0.0142	6.3	1.591	1.65
2	7.6	0.0284	4.9	1.508	1.56
3	11.4	0.0426	4.1	1.413	1.47
4	15.2	0.0568	4.0	1.273	1.32
6	22.8	0.0852	3.1	1.068	1.11
8	30.4	0.1136	2.5	0.829	0.86

Table 4. Effect of temperature

$[\mathrm{HCA}]_0 = 3.335 \times 10^{-5}$M; [TNB] = 0.02M;
$[\mathrm{H_2O}] = (3 \pm 1.5) \times 10^{-3}$M

T/K	$10^4k_{\mathrm{obs}}/\mathrm{s}^{-1}$	$(A_\infty - A_0)$
293.2	5.4, 6.5	1.776, 1.770
298.2	9.7[a]	1.856
307.5	15.0, 15.8	1.702, 1.771
313.2	19.6, 17.1	1.778, 1.806
318.2	22.6, 24.2	1.790, 1.820

[a] Result from Table 2.

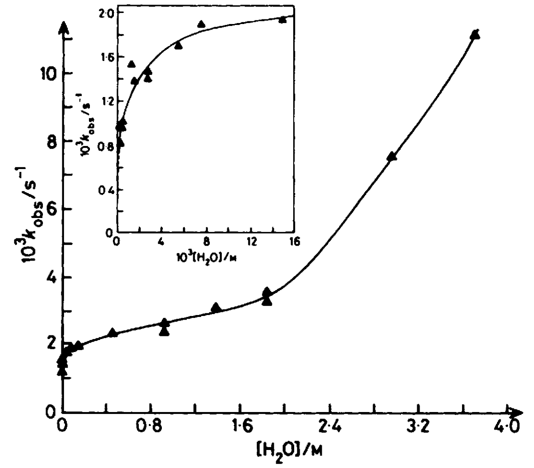


Figure 2. Dependence of rate constant on concentration of water (inset: expansion of low-concentration range)

(2φ) is calculated according to equation (5) from the corresponding ratio $(A_\infty - A_0)/\varepsilon_1[\mathrm{HCA}]_0$, where ε_1, the molar absorption coefficient at 431 nm, is taken to have the value[17] 2.89×10^4 mol^{-1} dm^3 cm^{-1}.

Table 2 gives a set of results for runs with solutions of constant TNB concentration but varying water content. The water concentrations have an uncertainty of *ca.* ±0.003M, which corresponds to the difference between the concentration found by titration of the solution in the cuvette after completion of reaction and the concentration corresponding to the amount of water introduced originally by the component stock solutions.

In an analogous set of experiments, various small amounts of concentrated aqueous hydrochloric acid were added to the reaction medium (Table 3). Small volumes of the acid were transferred to samples and reference cuvettes using an all-plastic 'Finnpipette'. The cells were septum-sealed before injection into each of 3 ml of 0.02M TNB solution in DMSO. Reaction was initiated by injection of 10 µl of a stock solution of HCA in dichloromethane.

A series of runs at different temperatures (Table 4) gave an activation energy of *ca.* 39 ± 2 kJ mol^{-1}; $\Delta S^\ddagger$ *ca.* -180 ± 10 J K^{-1} mol^{-1}.

Discussion

The reaction under observation is the formation of the coloured Meisenheimer adduct (**1**), identified by the agreement of the position of the u.v. absorption maxima with those of samples prepared from TNB by other reactions, either *via* proton abstraction from trichloromethane[20] or by decarboxylation of TCAA.[17] In some respects the process resembles the decomposition of TCAA in DMSO in the presence of TNB.[17] In particular, the rate of the reaction is independent of the concentration of TNB, which indicates that TNB scavenges a reactive species that is generated in earlier steps. However, the reaction of TCAA in DMSO is more rapid. At low concentrations of added water or acid the rate constant is approximately ten times greater. This suggests that the rate-limiting first-order process under observation is the breakdown of HCA, and that a concurrently formed molecule of TCAA then decomposes more rapidly to form the same product. In both cases the presence of TNB as scavenger for trichloromethanide anions suppresses the occurrence of other modes of destroying these ions. The liberation of TCAA in low concentration during the decomposition of HCA explains the use of HCA as a trichloroacetylating reagent under conditions where the acidity of the solution is required to remain low throughout.[4,7]

The formation of $\mathrm{CCl_3^-}$ as precursor in the production of trichloromethane from HCA in dimethylformamide solution had previously been suggested.[8] Small amounts of tetrachloromethane are also detected under these conditions and this has been attributed to the abstraction of positive chlorine from undecomposed HCA by trichloromethanide anions.[12] A free-radical mechanism has been put forward for the formation of tetrachloromethane from HCA in nitromethane solution.[9] At the low concentrations of HCA used in the present study (*ca.* 3×10^{-5}M) such reactions of an intermediate with a reactant molecule are not found.

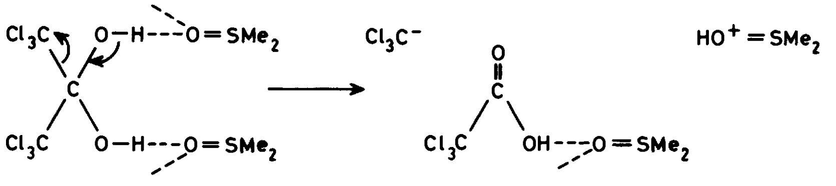
The reaction of HCA differs from that of TCAA in its dependence on the concentration of added water. Low concentrations of water have only a small effect on the decomposition of TCAA; the presence of 1M-water depresses the rate by *ca.* 30%. A corresponding addition of water trebles the rate of reaction of HCA from the value observed for the sample of DMSO dried and handled as described in the Experimental section. A plot of the value of the rate constant against the concentration of water (Figure 2) shows the existence of a complex relationship, and the results at low water concentrations are compatible with the supposition that the rate may drop to zero in the complete absence of water. We note also that at the highest concentrations of water studied the observed rate constant has a similar value to the rate constant for TCAA. That apparently simple first-order kinetics were found for HCA even under these conditions may be due to the fact that for these rapid reactions only the final part of the reaction was observable by the techniques used in this study.

A second important difference in the behaviours of HCA and TCAA is the much greater sensitivity of the rate of the latter reaction to added hydrochloric acid. The presence of 2.4×10^{-3}M-hydrochloric acid reduces the rate of reaction of TCAA to less than a fifth of the value found in the absence of added acid, whereas a similar concentration of acid would reduce the rate for HCA by perhaps 50% (see Table 3).

The heterolysis of HCA to form trichloromethanide anions and trichloroacetyl cations [equation (9)] is energetically improbable, whereas breakdown of the hydrate of HCA according to equation (10) is a more acceptable process. On this basis we can explain the effect of water as being due to the formation of the hydrate. From the shape of the curve in Figure 1, this hydration of HCA at a concentration of 3×10^{-5}M appears to be substantially complete at a water concentration of *ca.* 0.02M. The rate increase up to that concentration may then be attributed to the increase of the proportion of HCA that is present in solution as hydrate. The superimposed increase in rate which continues as the water concentration rises above *ca.* 0.2M has to be attributed to a different factor, most plausibly a medium effect on the rate of reaction (10). A more complete representation [equation (11)] of the breakdown of the hydrate would recognise the role of unusual hydrogen bonding between that species and DMSO.[21,22]

$$(Cl_3C)_2CO \longrightarrow Cl_3C^- + Cl_3CCO^+ \qquad (9)$$

$$(Cl_3C)_2C(OH)_2 \longrightarrow Cl_3C^- + Cl_3CCO_2H + H^+_{solv.} \qquad (10)$$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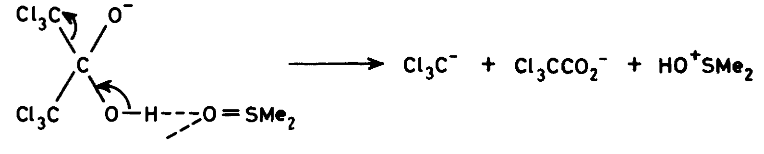
(12)

In the case of TCAA, the formation of CCl_3^- occurs only, or very predominantly, from the trichloroacetate ion. Addition of hydrochloric acid represses the ionization of the acid and therefore reduces the rate. By contrast, the effect of added acid on the HCA decomposition is relatively small and, on this basis, one would infer that the breakdown of the conjugate base of HCA hydrate [equation (12)] does not occur *much* more easily than that of the hydrate itself [equation (11)].

Of course, the hydrate of HCA is expected to be a very much weaker acid than TCAA, and the concentration of the conjugate base of HCA hydrate may accordingly be quite low even in the complete absence of added acid. Because this effect is so small, and superimposed on a larger and not quantitatively understood general medium effect on the reaction, we have not attempted to analyse the observed rate constants in terms of equilibrium and rate constants of component steps of the mechanism. The uncommonly large negative entropy of activation points to an increased importance of solvent–solute interactions in the transition state.

The observed effects of added water and of acid on the final concentration of the adduct (**1**) are to decrease the yield of (**1**) presumably by competition of reactions (13) and (14) with reaction (3). The effect of acid is less powerful in the case of HCA than for TCA under the different conditions of the respective experiments. (The concentration of water was appreciably higher for the experiments with TCAA.)

$$CCl_3^- + H_2O \longrightarrow CHCl_3 + OH^- \qquad (13)$$

$$CCl_3^- + H^+_{solv.} \longrightarrow CHCl_3 \qquad (14)$$

In the absence of added water the recorded values of 2φ are *ca.* 10% less than would have been expected on the basis of quantitative conversation of HCA into the adduct (**1**). This result is similar to observations with TCAA and may arise from direct proton transfer from TCAA to CCl_3^-.

Acknowledgements

We thank the Ain Shams University, Egypt, for granting leave of absence to W. N. W.

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Received 26*th June* 1985; *Paper* 5/1062