Thermochimica Acta, 105 (1986) 91–100
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A THERMOMETRIC STUDY ON THE STABILITY OF DI-BUTYL THIOUREA IN ACID SOLUTIONS *

A.M. SHAMS EL DIN and RASHEED A. ARAIN

Material Testing Laboratory, Water and Electricity Department, Abu Dhabi (United Arab Emirates)

(Received 24 January 1986)

ABSTRACT

Di-butyl thiourea (DBTU) reacts with moderately concentrated solutions of HNO_3 with the evolution of considerable heat. The reaction is examined by the thermometric technique. The temperature/time curves of the system first exhibit an induction period, followed by a rapid rise of temperature to a maximum value. Analysis of the results reveals that the reaction is bimolecular in DBTU and five order in HNO_3. It has an activation energy of 14 kcal mol^{-1}.

DBTU is very slowly decomposed by moderately concentrated solutions of HCl or H_2SO_4. The reaction is greatly enhanced when $K_2Cr_2O_7$ or $KMnO_4$ is present. No induction period is recorded under these conditions.

A mechanism accounting for the oxidation of DBTU, which satisfies all experimental findings, is suggested.

INTRODUCTION

The inhibitor di-butyl thiourea (DBTU), sold under the trade name "Stannine LTP", is used in the desalination plants of Abu Dhabi as an additive to the HCl acid wash of the condensers of the multi-stage evaporation distillers. In April 1983, four engineers suffered severe eye inflammations when they prematurely entered the brine heater water box of the distiller, following one such normal acid wash. The attack, which was felt a few hours after exposure, intensified with time and necessitated medical attention. One of the gentlemen experienced temporary blindness and was hospitalized for two days.

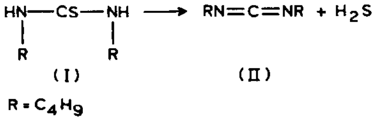
These features, together with the fact that neither skin irratation nor lung pains were felt, ruled out the possibility that the attacking agent was the acid itself. Since DBTU alone is stable, the substance causing eye irritation was

---

* Paper presented before the 6th European Symposium on Corrosion Inhibitors, Ferrara, Italy, September 16–20, 1985.

0040-6031/86/$03.50

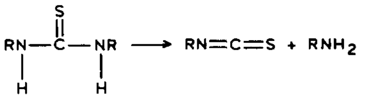
suspected to be one of the acid decomposition products of the additive. In fact an unofficial enquiry at ICI confirmed the possibility of DBTU decomposition. In mild acid or alkali, and at ambient or elevated temperatures, DBTU (**I**) in contact with CuO (tube surface), was considered to decompose to the di-butylcarbodiimide (**II**).



$$\underset{\text{(I)}}{\underset{R}{HN}\text{—CS—}\underset{R}{NH}} \longrightarrow \underset{\text{(II)}}{RN{=}C{=}NR} + H_2S \qquad (1)$$

$$R = C_4H_9$$

The mother compound, thiourea, is known to hydrolyze easily in acid solutions. Whilst organic text books describe hydrolysis to yield urea and H_2S [1], a recent publication assumes the product to be cyanamide $H_2N{-}C{=}N$ [2]. On the other hand, a number of authorities [3–5] consider that the attack of hydrochloric acid on thiourea leads to the formation of isothiocyanate. Extending this idea to di-butylthiourea it might be assumed that butylisothiocyanate is produced according to



$$\underset{H}{RN}\text{—}\overset{S}{\overset{\|}{C}}\text{—}\underset{H}{NR} \longrightarrow RN{=}C{=}S + RNH_2 \qquad (2)$$

In view of the meagre information available on the acid decomposition of DBTU, it appeared of interest to examine it in some detail. We have also confirmed the decomposition of DBTU when admixed with relatively concentrated acid solutions. The reaction is particularly vigorous, and is completed within a short time when the acid is HNO_3. The reaction is also accompanied by the evolution of considerable heat. We have, therefore, applied the thermometric technique [6–8] to study the effect of a number of variables on the stability of the additive. No work on DBTU from this stand point has hitherto been published.

EXPERIMENTAL

The reaction vessel and the experimental set up for registering thermometric curves were described earlier [6,9]. The total volume of the reaction mixture was 10.0 ml, and unless otherwise stated, the initial temperature was 29°C. The additive was used in its formulated form, and accordingly its concentration is expressed as volume percent. Temperature variations were recorded to ±0.5°C on an ordinary mercury thermometer. Experiments carried out under identical conditions were highly reproducible; with a deviation of ±0.5°C in the maximum temperature, and of ±1 min, in the time taken to reach it.

RESULTS AND DISCUSSION

The curves of Fig. 1 represent the variation of temperature with time of 10 ml portions of 6 M HNO_3 containing increasing concentrations (vol./vol.) of DBTU, varying between 5 and 35%. The initial temperature of this set of experiments, T_i, was 29°C. As is seen from the curves, the rise in temperature at the beginning is very slow, and the system passes through an induction period, whose length increases with decrease of the additive concentration in solution. Then, quite suddenly, the temperature rises quickly to attain a maximum value, T_m. In solutions $\geqslant$ 10% DBTU, T_m is practically independent of the additive concentration, and is very near to the boiling point. As the inhibitor content is further reduced, T_m progressively decreases, and the time to reach it increases. No detectable rise in temperature was recorded in HNO_3 solutions containing less than 5 vol.% of DBTU, within the time span of our experiments.

Curves having the same features as those depicted in Fig. 1 were also obtained when the experiments were conducted at other higher initial temperatures. Here, however, the induction periods were shorter, and the attainment of maximum temperatures was much faster than those seen in Fig. 1. In Fig. 2 this behaviour is represented for the case of 6 M HNO_3 solutions containing 15% DBTU.

The features of the curves of Figs. 1 and 2, and the like, namely the occurrence of an induction period, followed by a rapid rise in temperature to attain T_m, strongly suggest that acid decomposition of DBTU occurs as two consecutive steps, the first of which is rate determining. The decomposition

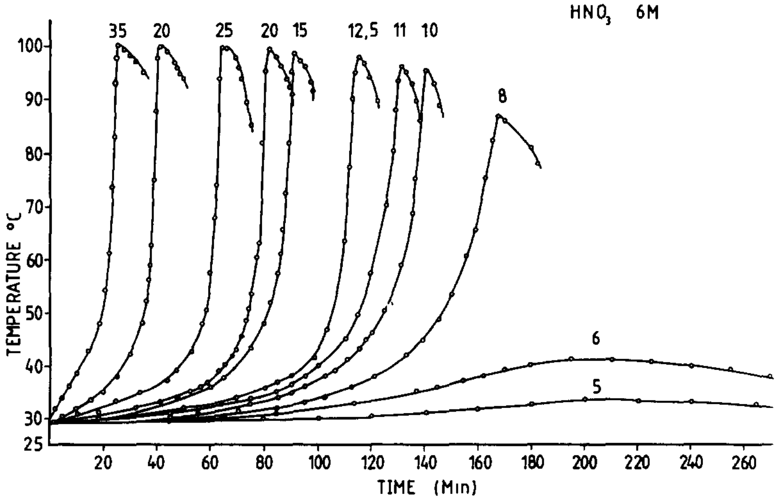


Fig. 1. Thermometric behaviour of DBTU in 6 M HNO_3. Numbers on the curves refer to vol.% of additive.

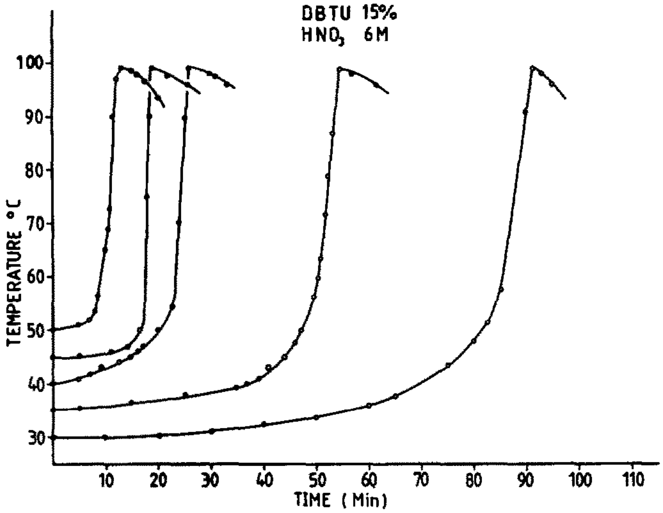


Fig. 2. Effect of the initial temperature on the thermometric curves of 15% DBTU in 6 M HNO_3.

can, therefore, be looked upon as being another example of "Clock reactions" [10]. That this is actually the case was proved as follows.

In solutions of the same acid concentration, the rate of decomposition of DBTU, R, can be expressed as

$$R = KC^n \tag{3}$$

where K is the rate constant, incorporating a proportionality factor converting volume percentages of DBTU into corresponding gram moles per litre, C is the concentration of the additive in volume percent and n is the order of the reaction with respect to DBTU. Further, it is considered that at the time, t, of registering T_m, all the DBTU has decomposed. The average rate R is equal to $R = C/t$. According to eqn. (3) at one and the same temperature, the plot of log R vs. log C should yield a straight line with a slope equal to n, thus establishing the order of the reaction. The line also intercepts the log R axis at the value of log K, enabling the calculation of the specific reaction rate.

In Fig. 3 plots of log R vs. log C are given for the decomposition of DBTU in 6 M HNO_3 at different initial temperatures varying between 29 and 50°C. Invariably straight lines are obtained which satisfy the general relation (3). The lines for 29 and 35°C are practically parallel, and have a slope equal to 2. This shows that the decomposition of DBTU is a bi-molecular reaction with respect to the additive. The other lines for initial temperatures of 40, 45 and 50°C, have somewhat lower gradients, amounting successively to 1.58, 1.64 and 1.70. Despite the fact that the values are lower

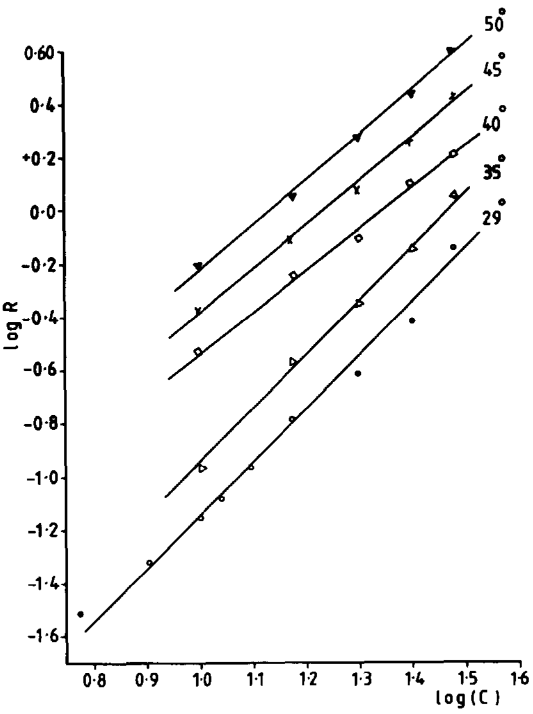


Fig. 3. Variation in the rate of decomposition of DBTU with additive concentration at different initial concentrations.

than expected, they leave little doubt regarding the bimolecular nature of the reaction at these temperatures too.

Measurement of the rate of decomposition of DBTU at different temperatures allows the evaluation of the activation energy of the reaction. This is done by plotting log K under the same conditions as a function of the reciprocal of the absolute temperature, whereby a straight line is obtained, in accordance with the familiar Arrhenius relationship

$$R = B \exp(-\Delta H/RT) \tag{4}$$

From the curves of Fig. 3, the rate constants K at $C = 1$ were computed. However, when these were plotted as a function of $1/T$, the points did not fall on one line, as expected.

This non-linearity is apparently the result of the fact that the lines of Fig. 3 are not completely parallel. The deviation from linearity is also more pronounced because of the large extrapolation involved, here to log $C = 0$. This difficulty is overcome by constructing log $K - 1/T$ curves from actual data for solutions of the same DBTU concentrations. The curves making the best fit to these points allow the evaluation of the most appropriate activation energy of the decomposition reactions. The lines of Fig. 4 repre-

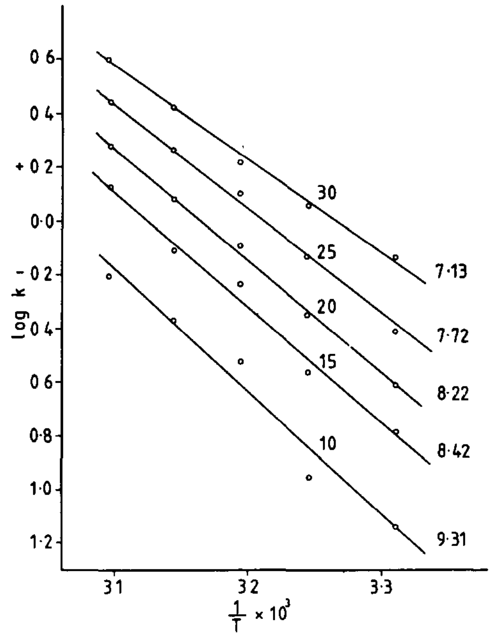


Fig. 4. Variation in the rate of decomposition of solutions of 10, 15, 20, 25 and 30 vol.% DBTU with 1/Tabs. Numbers on the right side of curves are average activation energies.

sent the set of curves thus obtained for solutions of concentrations varying between 10 and 30% DBTU.

It can be seen that the gradients of the lines, and hence the ΔH values, decrease progressively as the concentration of the organic compound is increased. A plot of the ΔH values thus obtained as a function of log C (not shown) was fairly well represented by a straight line. When extrapolated to log $C = 0$ this yielded the required $\Delta H°$ value of the decomposition reaction which was 14.05 kcal mol^{-1}.

The curves of Fig. 5 represent the thermometric behaviour of mixtures containing 15% DBTU in HNO_3 solutions of different concentrations. As is evident, a decrease in the acid strength is accompanied by a corresponding increase in the induction period. On the other hand, the maximum temperature, T_m developed in the reaction decreases at a rate of ~ 1°C mol^{-1} HNO_3. Analysis of the curves of Fig. 5 in the manner given above to determine the order of reaction with respect to the acid was similarly carried out. Within the concentration range examined, a fairly good straight line was obtained for the log R/log C relationship, the slope of which suggested a reaction of order 5. This high value is indicative of the complexity of the reaction. As has been mentioned above, the reaction between DBTU and HNO_3 involves in all probability oxidation of the additive. The exact mechanism by which this degradation occurs is not yet fully understood, but participation of the NO_3^- ion is quite certain. Reduction of the NO_3^- ion

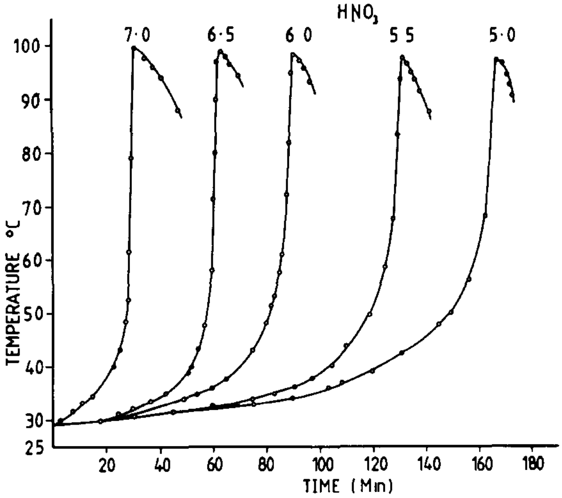


Fig. 5. Thermometric behaviour of 15 vol.% DBTU in HNO_3 of different concentrations.

involves the uptake of H^+ ions, the number of which depend on the final valency state of the reduction product. This, together with the probable involvement of protons in subsequent steps of DBTU decomposition would account for the high order of reaction computed for HNO_3.

The reaction between DBTU and solutions of HCl or H_2SO_4 of comparable concentrations was too slow to be followed by the thermometric technique.

Since these acids are equally strong, their slowness in decomposing the additive is apparently connected with lack of the oxidizing properties of HNO_3. One can safely conclude, therefore, that the reaction between DBTU and HNO_3 is primarily an oxidation reaction. Support for this idea comes from the results of experiments in which strong oxidizing agents were added to solutions of HCl and H_2SO_4.

The curves marked O in Fig. 6 reveal that no temperature rise was recorded when admixing 15% DBTU with 4 M HCl or 1.5 M (3N) H_2SO_4. When the first solution contained additions of $K_2Cr_2O_7$, an instantaneous rise in temperature was noted. The maximum measured temperature, T_m, varied with the oxidant content in the medium, Fig. 6A. On the other hand, when keeping the oxidant concentration the same, T_m changed proportionally with the acid molarity (Fig. 6B). In both sets of experiments the amber red colour of the dichromate changed into the green colour characteristic of the chromic ion.

Again, one cannot escape the conclusion that the evolution of heat was connected with the oxidation of the organic compound, and that the reaction involved the participation of H^+ ions. Results similar to those described above were also obtained when $KMnO_4$ was added in increasing

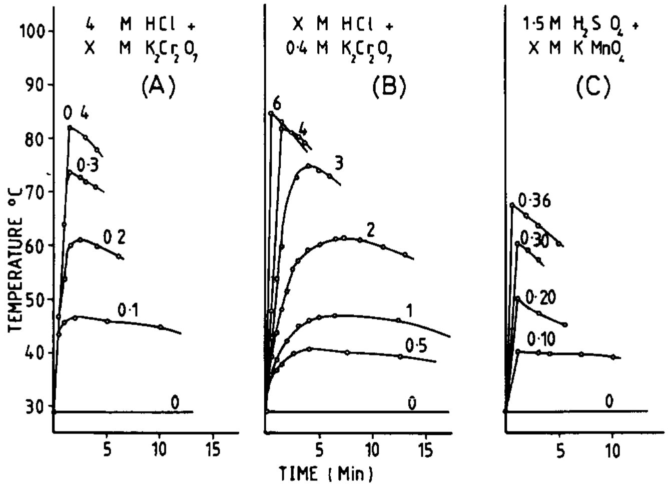


Fig. 6. Thermometric behaviour of 15 vol.% DBTU in 4 M HCl (A, B) and 1.5 M H_2SO_4 (C), with additions of $K_2Cr_2O_7$ and $KMnO_4$ (see text).

concentrations to H_2SO_4 solutions, Fig. 6C. At and beyond the points of maximum temperatures, the pink colouration of the permanganate was fully discharged. The interesting feature of the curves of Fig. 6 is the complete absence of the induction period; the temperature rises directly from the moment of admixing the oxidizing agent with the acid solutions containing the inhibitor. The reason for that is quite apparent. Whilst oxidation of DBTU with $K_2Cr_2O_7$ or $KMnO_4$ is ionic in character, that with HNO_3 is molecular in nature, involving first the breaking of N–O bonds and the release of active oxygen.

It should be noted that mixtures of DBTU and the two acids HCl or H_2SO_4 (in the absence of oxidants) also show clear indications of inhibitor decomposition, when left for long enough times. Whether the degradation of the organic compound follows the same route as that recorded under oxidative conditions, or is due to a completely different mode of decomposition (e.g. hydrolysis to the corresponding urea derivative) is difficult to conclude from the results of the present investigation. It is not unlikely, however, that the slow decomposition of DBTU is the result of oxidation by molecular oxygen of the atmosphere.

This idea might account for the break down of the additive inside the distiller during the acid wash. Since cleaning of the tubes is normally carried out at moderate temperatures (50–55°C) an acceleration of the reaction might be expected. The inside of the tubes usually carry a layer of cupric oxide (from the alloy material) and ferric oxide (deposited from the sacrificial anodes). When dissolved during the acid wash, both Cu^{2+} and Fe^{3+} ions, being mild oxidizing agents, can catalyze the oxidation of DBTU.

Experiments in which $FeCl_3$ (up to 2 M) was added to 6 M HCl, or in which $CuSO_4$ (up to 1 M) was added to 6 M H_2SO_4, both containing 15% DBTU were carried out. An instantaneous increase in the temperature upon mixing the components of the system of ca. 2–4°C were recorded. These values were some 0.5 to 1.0°C higher than those measured in the absence of the metal ions, and are thus within the experimental limits of accuracy of temperature measurement. No definite conclusion can therefore be based on these results, and the suggested mechanism remains open for further confirmation by other techniques.

MECHANISM OF DECOMPOSITION OF DBTU

Although the thermometric technique has not been used to elucidate mechanisms of chemical reactions, the results of the present investigation allow certain conclusions to be drawn which shed some light on the decomposition of DBTU in HNO_3 solutions. Thus, for example:

(a) the additive reacts vigorously with HNO_3 solutions with the evolution of considerable heat. Equimolar concentrations of HCl or H_2SO_4 do not affect decomposition to any measurable extent. This fact rules out hydrolysis of the thio compound to the corresponding urea derivative as a cause of the high temperatures evolved. Hydrolysis of thiourea occurs in solution of the three mineral acids to the same extent [1].

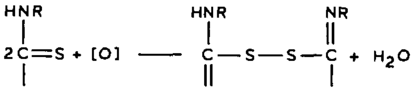
(b) That the reaction of DBTU and HNO_3 is primarily an oxidation reaction is proved by the results of experiments with HCl or H_2SO_4 containing additions of strong oxidizing agents. Under these conditions an instantaneous rise in temperature is recorded.

(c) The reaction of DBTU with HNO_3 solutions is bimolecular with respect to the organic compound, and is of a high order with respect to the acid itself. It has an activation energy of 14 kcal mol^{-1}.

(d) Unsubstituted thiourea decomposes in solutions of HNO_3 in a manner very similar to that noted with DBTU [11].

The decomposition of simple thiourea in acid solutions containing $FeCl_3$ was studied by Bogenschutz and co-workers [12]. Through IR spectral analysis it was concluded that thiourea was quickly converted into dithioformamidine.

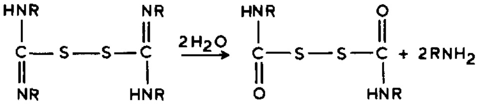
Assuming that substitution with butyl groups would only affect the rate but not the route of the reaction, the following mechanism for decomposition of DBTU is formulated by analogy [11] as



$$2\,(HNR)_2C{=}S + [O] \longrightarrow (HNR)(RN{=})C{-}S{-}S{-}C({=}NR)(HNR) + H_2O \qquad (5)$$

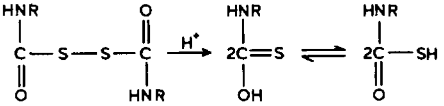
(I) (III)

Compound (**III**), with two imine groups, readily hydrolyzes to the corresponding diaminocarbonyl disulphide (**IV**). Acid hydrolysis of (**IV**) proceeds readily to yield butyl thiocarbamic acid (**V**).



(III) (IV)

(6)



(IV) (V) (V′)

(7)

Like a large number of thio organic compounds, the butyl thiocarbamic acid (V) or its thiol isomer (V′) is expected to possess lacrymatic properties, and is assumed to be the cause of the eye inflammation accident which took place in the Abu Dhabi Plant.

REFERENCES

1 I.L. Finar, Organic Chemistry, Vol. 1, Longman, London, 1971, p. 422.
2 D.M.A. Nawab, Bangladesh J. Sci. Ind. Res., 10 (1975) 163.
3 H. Ulrich and R. Richter, in S. Patai (Ed.), Chemistry of Functional Groups, Wiley, New York, 1977; L. Drobnica, P. Kristian and J. Augustin, p. 1043.
4 J.N. Leconte and L.H. Chance, J. Am. Chem. Soc., 71 (1949) 2240.
5 N.I. Volinkin, Zh. Obshch. Khim., 37 (1957) 483.
6 K. Aziz and A.M. Shams El Din, Corr. Sci., 5 (1965) 489.
7 A.M Shams El Din and J.M. Abd El Kader, Oberfl. Surface, 18 (1977) 11.
8 A.T. Kuhn and A.M. Shams El Din, Surface Technol., 20 (1983) 55.
9 A.M. Shams El Din, Proc. 5th Int. Corr. Congr., Tokyo, 1972, p. 1078.
10 Practical Physical Chemistry, Univ. Cairo Pub. Centre, 1969, p. 81.
11 A.M. Shams El Din, A.A. El Hosary, R.M. Saleh and J.M. Abd El Kader, Werkst. Korros., 28 (1977) 26.
12 A.F. Bogenschutz, C. Heinz and J.L. Jostan, Metalloberfl., 28 (1974) 397.