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THE CHEMICAL EFFECTS OF STORING HYDRAZINE CONTAINING CARBON DIOXIDE IMPURITY IN STAINLESS STEEL SYSTEMS

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ABSTRACT

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The effect of low concentrations (<250 ppm) of dissolved carbon dioxide (carbazic acid) on the rate of decomposition of hydrazine, in both stainless steel and glass vessels, has been investigated. In a stainless steel vessel at 60°C the rate of hydrazine decomposition was found to be directly proportional to the total concentration of added carbon dioxide (above about 20 ppm) while for a glass vessel at 51°C the relationship between concentration of added carbazic acid and hydrazine decomposition rate is best interpreted in terms of a Langmuir isotherm equation. The preparation of some carbazato-complexes of iron, chromium and nickel, such as may be formed during the hydrazine/carbon dioxide corrosion of stainless steel, is also reported. Additions of small amounts of dicarbazatodihydrazineiron (II) to hydrazine in a glass vessel had no measurable effect on the decomposition rate at 43°C. Tricarbazatochromium (III) dihydrate was found to be similarly inactive while the principal nickel carbazato- complex is completely insoluble in hydrazine.

INTRODUCTION

Previous investigations by other workers (refs. 1 and 2) have indicated that the presence of relatively small amounts (∿100 ppm) of carbon dioxide impurity in hydrazine in contact with stainless steel can lead to significant metal corrosion and to an increase in the concentration of dissolved metal ions. The process is accompanied by a corresponding increase in the rate of homogeneous decomposition of hydrazine (as measured in glassware) into nitrogen and ammonia (ref. 3). This has important consequences for the use of hydrazine as a rocket propellant since the production of nitrogen, which is largely insoluble in hydrazine, leads to a build-up of ullage pressure in closed vessels and may therefore limit the storage life of stainless steel systems.

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The involvement of carbon dioxide in promoting stainless steel corrosion by hydrazine and the consequent increase in propellant decomposition rate has prompted the suggestion (ref. 2) that certain transition metal complexes, involving ligands derived from hydrazine and carbon dioxide, may function as homogeneous catalysts for the decomposition of hydrazine. Carbon dioxide itself, which dissolves in hydrazine to give carbazic acid,

$$2\ N_2H_4 + CO_2 \rightarrow N_2H_5^+ \cdot N_2H_3CO_2^-$$

is also claimed to be an effective catalyst (ref. 4).

In order to understand more fully the role of carbon dioxide in the corrosion process and to assess its effect, in conjunction with metal ions, on the rate of hydrazine decomposition kinetic measurements have been made on CO_2-doped hydrazine in stainless steel and glass vessels. In addition, carbazato- complexes of the principal component metals of stainless steel (iron, chromium and nickel) have been prepared and the effect of certain of them on the hydrazine decomposition rate has been investigated.

EXPERIMENTAL

Hydrazine used in the decomposition rate studies conformed to US Monopropellant Grade specification (ref. 5). All manipulations involving the loading of hydrazine into stainless steel or glass vessels and the addition of CO_2 and metal complex dopants were conducted in a nitrogen-filled glove-box.

The analysis of carbon dioxide in hydrazine was carried out using a gas chromatographic method developed at the Jet Propulsion Laboratory, Pasadena (ref. 2). Hydrazine samples were analysed for trace metal ions using atomic absorption spectroscopy. Microanalysis (C,H,N) of metal complexes was performed by PERME, Waltham Abbey.

All decomposition rate measurements on hydrazine were carried out using closed glass or stainless steel vessels fitted with strain gauge pressure transducers and housed in thermostatically-controlled hot-air ovens. These assemblies and the method by which the decomposition rate (as scc of nitrogen per day) was calculated from the observed rise in ullage pressure have been described previously (ref. 6).

Preparations

Hydrazinium tricarbazatoferrate (II) hydrate

This was adapted from the method given by Braibanti et al (ref. 7).

Ferrous sulphate (5.56 g, 0.02 mol) was dissolved in water (10 cm^3) under a continuous flow of nitrogen and excess anhydrous hydrazine (5 cm^3) was added. Carbon dioxide was bubbled through the solution with the nitrogen until the original precipitate had dissolved to give a green solution. The solution was then left for two days to crystallise. The crystals of the complex were filtered-off in a glove-box under nitrogen and dried in a vacuum desiccator.

Dicarbazatodihydrazineiron (II)

Hydrazinium tricarbazatoferrate (II) hydrate (2.3 g) was added to anhydrous hydrazine (20 cm^3) and the solution was shaken. The pale blue precipitate of the complex which was formed was filtered-off under nitrogen, washed with methanol and dried in a vacuum desiccator.

Tricarbazatochromium (III) dihydrate

Chromium (III) chloride (2.66 g, 0.01 mol) was dissolved in water (10 cm^3) under a continuous flow of carbon dioxide and the solution stirred and heated until simmering. Anhydrous hydrazine (2 cm^3) was then added dropwise. The solution was stirred and heated for a further three hours under a continuous flow of carbon dioxide. The blue precipitate was filtered-off and the red filtrate left to cool and crystallise for three days. The red crystals of the complex were then filtered-off, washed with methanol and dried under vacuum.

Dicarbazatohydrazinenickel (II)

Nickel (II) chloride hexahydrate (2.38 g, 0.01 mol) was dissolved in anhydrous hydrazine (70 cm^3) and the solution set aside, open to the atmosphere, for two months. At the end of this time violet crystals of the complex had been deposited. These were filtered-off, washed thoroughly with water then methanol and dried under vacuum.

TABLE 1

Microanalytical data

Complex	% Found			% Required		
	C	H	N	C	H	N
$[N_2H_5][Fe(N_2H_3CO_2)_3]\cdot H_2O$	10.9	5.0	33.9	10.8	4.8	33.7
$Fe(N_2H_3CO_2)_2(N_2H_4)_2$	8.9	5.2	41.0	8.9	5.2	41.5
$Cr(N_2H_3CO_2)_3\cdot 2H_2O$	11.5	4.1	26.8	11.7	3.9	26.8
$Ni(N_2H_3CO_2)_2 N_2H_4$	9.9	4.2	34.8	10.0	4.2	34.9

RESULTS AND DISCUSSION

Effect of dissolved carbon dioxide on the decomposition rate of hydrazine in a stainless steel vessel

The vessel used in this investigation had an internal volume of 1348 cm^3 and was fabricated from 304L low-carbon stainless steel. While this particular steel is widely used for hydrazine containment (ref. 8) there is evidence that its corrosion rate is dependent upon the carbon dioxide content of the propellant (ref. 2). The volume of hydrazine contained in the vessel was held at around 1209 cm^3 throughout the series of kinetic runs, thus maintaining an ullage of approximately 11% (at 20°C) for the total assembly including the pressure transducer.

The decomposition rate at 60°C for each of five hydrazine loadings was determined by measuring the rise in ullage pressure, as indicated by the transducer, and converting this to the rate of nitrogen generation (assuming $3\ N_2H_4 \rightarrow N_2 + 4\ NH_3$) using methods previously described (ref. 6). The carbon dioxide content of the hydrazine was increased after each run by a nominal 50 ppm. This was achieved by removing an appropriate volume of hydrazine from the 304L vessel (approx 50 cm^3) and replacing it by a similar volume from a stock of heavily CO_2-doped hydrazine.

It was noticeable that, immediately following each addition of carbon dioxide, the rate of rise in ullage pressure at 60°C was higher but decreasing somewhat and only after a period of time (several weeks for 81 ppm carbon dioxide in hydrazine) did it settle down to an approximately constant value. A repeated number of measurements were therefore necessary for each hydrazine loading to ensure that steady conditions had been achieved. The initial high rate of pressure rise is interpreted as being due to the generation of nitrogen following attack of 304L by carbazic acid. It is this process which results in the observed increase in metal ion concentration in hydrazine (ref. 1).

The experimental results given in TABLE 2 reveal a definite correlation between carbon dioxide concentration and the decomposition rate of hydrazine in a 304L vessel at 60°C. However, for high carbon dioxide levels, the table shows a

TABLE 2

Carbon dioxide concentrations and hydrazine decomposition rates in the 304L vessel

CO_2 added (ppm)	Total (nominal) CO_2 conc. (ppm)	Rate of N_2 gen. at 60°C (scc day^{-1})	Post-run analyses (ppm)			
			CO_2	Fe	Cr	Ni
Nil	(29)	0.6	29	1	-	trace
50	79	4.2	81	8	trace	1
50	129	8.4	131	6	1	1
50	179	11.8	163	14	3	2
50	229	15.9	179	18	2	2

discrepancy between the nominal CO_2 concentration and the post-run concentration as determined by the JPL method (ref. 2). This can be explained (assuming no errors during the doping stage) by postulating the formation of metal carbazato-complexes which effectively bind the carbon dioxide and render it inaccessible under the conditions of the analysis procedure. The relatively high dissolved metal content of hydrazine to which has been added high levels of carbon dioxide (TABLE 2) supports this view. If it is assumed (vide infra) that iron, chromium and nickel dissolve in hydrazine, under the influence of CO_2, solely to give Fe $(N_2H_3CO_2)_2$ $(N_2H_4)_2$, Cr $(N_2H_3CO_2)_3$ and Ni $(N_2H_3CO_2)_2$ N_2H_4 , respectively, then a simple calculation reveals that 18 ppm of iron, 2 ppm of chromium and 2 ppm of nickel will account for 36 ppm of CO_2, bound as carbazate. This figure, when added to the 179 ppm found in the post-run analysis for run 5 (TABLE 2), gives a total of 215 ppm CO_2. This is close to the nominal value of 229 ppm. The point serves to emphasise the distinction, which has previously been made (ref. 1) between labile and non-labile carbon dioxide in hydrazine. It also makes clear that, in the presence of dissolved metal ions, the most widely used method for the analysis of CO_2 in hydrazine may not be very reliable.

When carbon dioxide dissolves in hydrazine the hydrazinium ion, $N_2H_5^+$, is formed together with an equal amount of carbazate ion, $N_2H_3CO_2^-$. It is of course the concentration of the latter (as the free ion) which is measured by the present 'carbon dioxide' analysis techniques (ref. 1), whereas the evidence indicates that the hydrazinium ion is the more important species with respect to stainless steel corrosion (ref. 4). It may be expected therefore that any precise correlation between the concentration of carbon dioxide in hydrazine and the propellant decomposition rate in a stainless steel vessel is likely to involve the total CO_2 concentration since that is equivalent to the concentration of added $N_2H_5^+$. This is demonstrated in FIGURE 1 which, using values from TABLE 1, reveals a linear relationship between total (nominal) carbon dioxide concentration and the hydrazine decomposition rate in the 304L vessel at concentrations above about 20 ppm carbon dioxide.

One interpretation of the correlation revealed by FIGURE 1 is that the hydrazinium ion is functioning as a catalyst for the decomposition of hydrazine at the metal surface. However, measurements in glassware on a sample of hydrazine from the final loading of the 304L vessel revealed that the decomposition rate fell by only 20% relative to the rate in stainless steel. It can be concluded therefore that the observed increase in hydrazine decomposition rate in the 304L vessel is largely the result of a homogeneous catalysed reaction, discounting the somewhat higher rates immediately after CO_2 addition.

Studies involving the addition of carbazic acid to hydrazine in a glass vessel (vide infra) show that there is no linear correlation between carbazic acid content and hydrazine decomposition rate in glassware. Therefore it is unlikely that hydrazinium ion can itself be functioning as an effective homogeneous decomposition catalyst in a stainless steel vessel. A consistent interpretation of the existing data would be that carbazic acid reacts with 304L to release a mild decomposition catalyst (probably a metal complex) into the hydrazine and that the catalytic activity of this species increases markedly, in a linear fashion, with the concentration of hydrazinium ion. A similar explanation has in part been put forward by Williams (ref. 9).

Preparation of metal carbazato- complexes

When carbazic acid in hydrazine attacks stainless steel it is likely that the products of the corrosion process, leeched into solution, are metal co-ordination complexes of hydrazine and the carbazate ion. Such complexes are known to exist (ref. 7) and it is possible that one or more of them may be playing a part in the catalysed homogeneous decomposition of hydrazine in stainless steel vessels. Accordingly, a range of carbazato- complexes has been prepared with iron, chromium and nickel as the central metal ions.

The iron complex, hydrazinium tricarbazatoferrate (II) hydrate, was prepared in aqueous hydrazine by a method adapted from that of Braibanti et al (ref. 7). The complex crystallised as pale green prisms that turned brown on exposure to air. This suggests that iron is present in the +2 oxidation state although no further investigations were carried out to establish this. Microanalytical data (TABLE 1) confirm the proposed formula. Attempts at replacing the hydrazinium counter cation by the tetramethylammonium ion were unsuccessful.

On its addition to hydrazine the tricarbazatoferrate (II) complex broke down to give carbazic acid and dicarbazatodihydrazineiron (II):

$$[N_2H_5][Fe(N_2H_3CO_2)_3]\cdot H_2O + 2\ N_2H_4 \rightarrow N_2H_5^+\ N_2H_3CO_2^- + Fe(N_2H_3CO_2)_2(N_2H_4)_2 + H_2O\ .$$

Therefore in the presence of carbon dioxide impurity iron is likely to exist in hydrazine solution as dicarbazatodihydrazineiron (II). The compound is pale blue and very air-sensitive, crystals turning brown within an hour of exposure to the atmosphere. The solid is not very soluble in hydrazine; however precipitation does not occur below the equivalent of about 700 ppm of iron.

When stainless steel is immersed in hydrazine and the vessel left open to the atmosphere the hydrazine takes on a red colouration after a period of time (ref. 8). It is now apparent that this colour is due to the formation of tricarbazatochromium (III). This complex, which is extremely soluble in hydrazine, was prepared as red crystals of the dihydrate by the reaction between chromium (III) chloride and carbon dioxide in aqueous hydrazine. The crystals are insoluble in water and dilute acid.

A nickel carbazato- complex was readily obtained by dissolving nickel (II) chloride hexahydrate in anhydrous hydrazine and allowing the solution to stand for several months open to the atmosphere. Violet crystals of dicarbazatohydrazinenickel (II) were formed (TABLE 1). The crystals are completely insoluble in hydrazine.

Effect of some soluble metal carbazato- complexes on the decomposition rate of hydrazine in glass vessels

In an attempt to identify the catalyst (derived from stainless steel) for the homogeneous decomposition of hydrazine, metal carbazato- complexes were added to samples of the Monopropellant Grade material in glass vessels and measurements of the resultant decomposition rates were made under controlled conditions.

Perhaps the complex most likely to act as a catalyst for hydrazine decomposition is dicarbazatodihydrazineiron (II) which is the form that dissolved iron probably takes in CO_2-contaminated hydrazine. The existence of an Fe (II)/Fe (III) couple might enable redox reactions to take place in hydrazine that would amount to a catalytic cycle for hydrazine decomposition. However, the addition of increasing amounts of the complex to about 80 g of hydrazine in a glass tube at 43°C produced no increase in decomposition rate (TABLE 3). Although dicarbazatodihydrazineiron (II) is not very soluble it was possible to dissolve up to 270 mg in the 80 g of hydrazine. It must be concluded therefore that iron, at least in the form of the added complex, does not take part in the catalytic cycle which is responsible for the observed homogeneous decomposition of hydrazine at temperatures in the range 40°C-60°C. This contrasts with findings at 171°C (ref. 4).

TABLE 3

Effect of dicarbazatodihydrazineiron (II) additions on the decomposition rate of hydrazine at 43°C

Added weight of complex (mg)	Concentration of dissolved iron (ppm)	Rate of N_2 gen. at 43°C (scc day^{-1})
0	-	0.11
2	5	0.09
5	13	0.09
9	23	0.11
11	28	0.11
31	80	0.09
51	132	0.11
112	290	0.09
133	345	0.09
156	404	0.10
186	482	0.10
214	554	0.11
269	697	0.10

The addition of about 5 mg of the complex tricarbazatochromium (III) dihydrate to hydrazine in a glass tube at 60°C also failed to produce an increase in propellant decomposition rate relative to the undoped hydrazine. Although further studies need to be carried out in this case, the initial indications are that chromium (III) is not active as a homogeneous catalyst for hydrazine decomposition.

Dicarbazatohydrazinenickel (II) is not sufficiently soluble in hydrazine to warrant investigation of its homogeneous catalytic activity with respect to hydrazine decomposition.

Effect of carbazic acid on the decomposition rate of hydrazine in a glass vessel

The addition of hydrazinium tricarbazatoferrate (II) hydrate to hydrazine has been shown to produce carbazic acid and dicarbazatodihydrazineiron (II). Since the latter was found to be inactive as a hydrazine decomposition catalyst in glass vessels the addition of hydrazinium tricarbazatoferrate (II) hydrate effectively becomes a means of doping hydrazine with carbazic acid. The addition of carbazic acid as a solid in this way can enable its concentration to be controlled with some precision so that reliable conclusions about its effect on hydrazine decomposition rates in glassware can be drawn.

Carbazic acid is an electrolyte in hydrazine and thus it is possible that, at low concentrations, it will have an effect on the decomposition rate by changing the ionic strength of the hydrazine solution in accordance with Debye-Hückel theory. However it has been found (ref. 10) that potassium iodide, a typical ionic material which is soluble in hydrazine, had no effect on the hydrazine decomposition rate at 43°C and therefore it can be assumed that any influence of carbazic acid will not be due to changes in ionic strength.

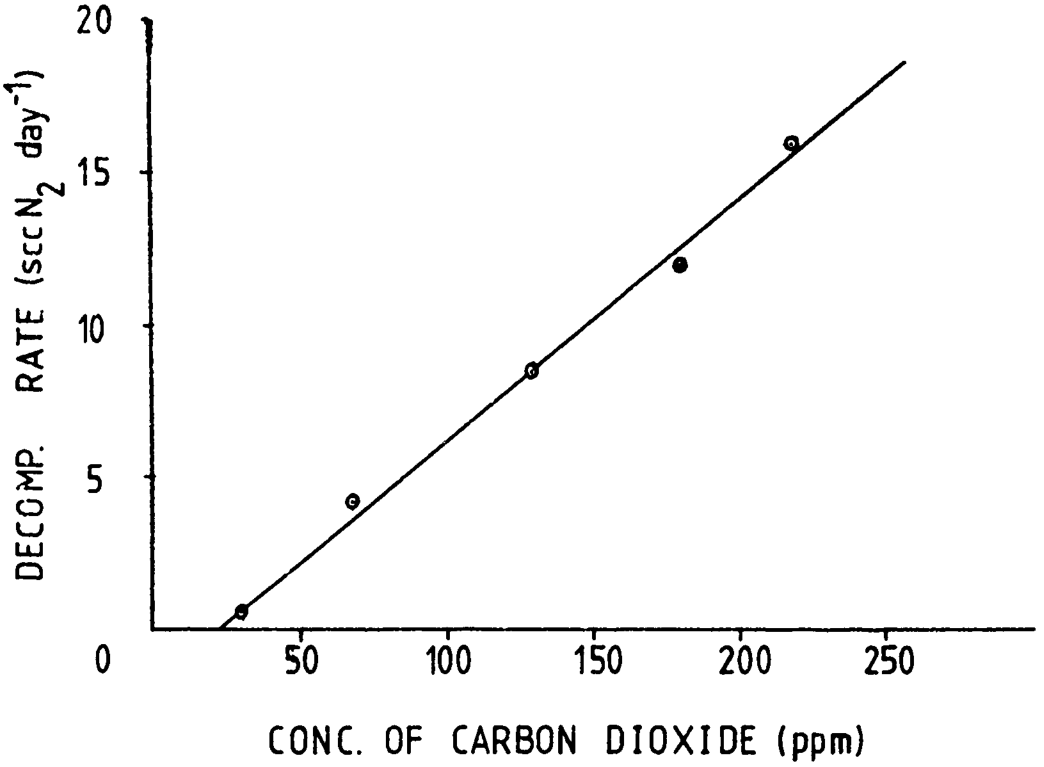
Results from an experiment in which carbazic acid (as $[N_2H_5][Fe(N_2H_3CO_2)_3]\cdot H_2O$) was added to hydrazine in a glass vessel at 51°C are given in TABLE 4. The

TABLE 4

Effect of carbazic acid on the decomposition rate of hydrazine in a glass vessel at 51°C

Added weight of iron complex (mg)	Concentration of dissolved CO_2 (ppm)	Rate of N_2 gen. at 51°C (scc day^{-1})
0	5	0.03
14	27	0.08
20	38	0.09
41	71	0.10
60	102	0.11
82	137	0.11
104	173	0.11

FIGURE 1. PLOT OF HYDRAZINE DECOMPOSITION RATE IN A 304L VESSEL AT 60°C AGAINST TOTAL CONC. OF DISSOLVED CARBON DIOXIDE



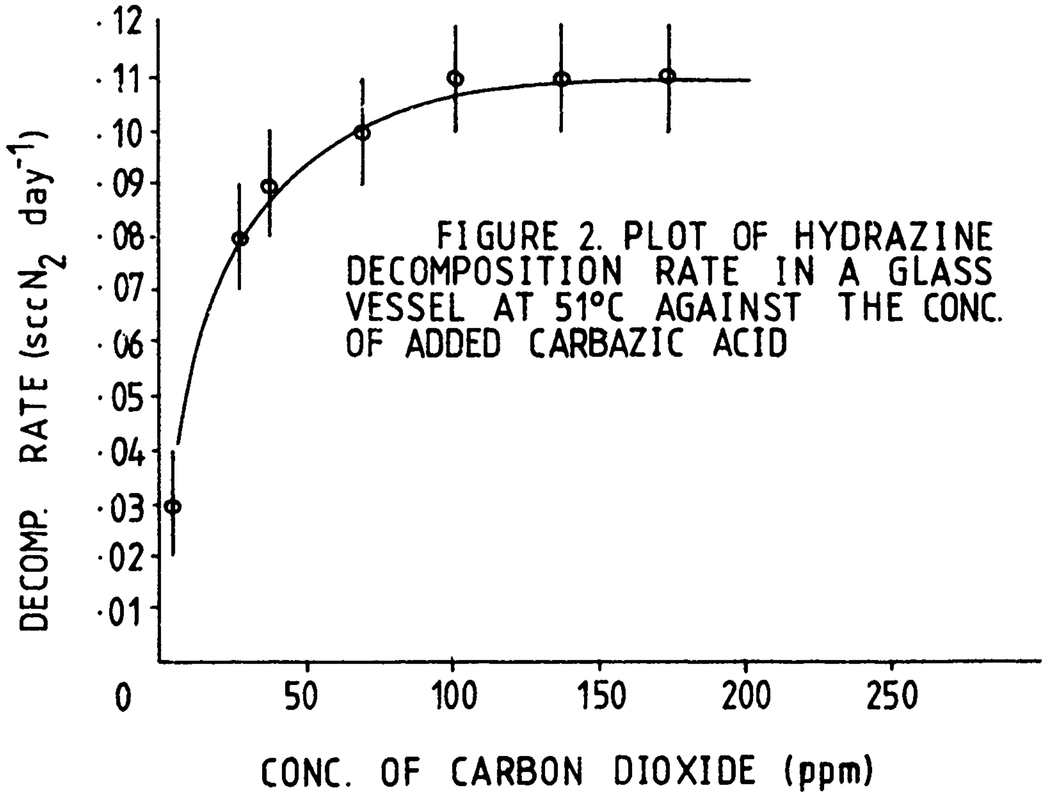


FIGURE 2. PLOT OF HYDRAZINE DECOMPOSITION RATE IN A GLASS VESSEL AT 51°C AGAINST THE CONC. OF ADDED CARBAZIC ACID

original hydrazine contained 5 ppm of carbon dioxide. A graph derived from the results is presented in FIGURE 2 and indicates that, unlike in a stainless steel vessel, carbon dioxide has little effect on hydrazine decomposition rates in a glass vessel. The probable reasons for this have already been discussed.

The relationship between CO_2 concentration and hydrazine decomposition rate as revealed in FIGURE 2 is typical of a surface catalysed reaction in which the rate is dependent upon the fraction of surface covered by the catalyst, this fraction being itself related to the concentration in solution by the Langmuir isotherm. In glass vessels, therefore, it appears that dissolved CO_2 promotes a surface catalysed reaction but that saturation surface coverage is achieved at very low levels of carbon dioxide and catalytic activity is thus not very marked The decomposition catalyst, leeched from a 304L vessel and whose activity is linearly dependent upon hydrazinium ion concentration, is clearly not present in the hydrazine used for this experiment in a glass vessel.

SUMMARY AND CONCLUSIONS

The addition of controlled amounts of carbon dioxide to hydrazine in a 304L stainless steel vessel at 60°C has revealed a linear relationship between hydrazine decomposition rate and total carbon dioxide concentration (above about 20 ppm). The failure to find a similar relationship in a glass vessel has led to the conclusion that a hydrazine decomposition catalyst is leeched out of 304L under the influence of dissolved carbon dioxide and that the activity of this catalyst increases linearly with hydrazinium ion concentration (equivalent to the total CO_2 concentration). Attempts at identifying this catalyst by adding carbazato- complexes of iron and chromium to hydrazine have met with no success.

The straight line obtained by plotting hydrazine decomposition rate in a 304L vessel against concentration of added CO_2 does not extrapolate back through the origin. Instead there appears to be a 'threshold' carbon dioxide value of about 20 ppm below which the decomposition rate remains low. This finding is consistent with previous work carried out on 304L (ref. 2) and suggests that a reduction in the specification for CO_2 in hydrazine from the existing 200 ppm down to about 20 ppm would be of considerable benefit, particularly in relation to the storage life of stainless steel systems.

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