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The Role of Hydroxamic Acids in the Retention of Fission Products in TBP Diluents. A Quantitative Study in a Model System

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The Role of Hydroxamic Acids in the Retention of Fission Products in TBP Diluents. A Quantitative Study in a Model System

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Abstract

The degradation with nitric acid of kerosene-type diluents of TBP in the reprocessing of nuclear fuel leads to the formation of primary nitroalkanes. These, under acid conditions, may hydrolyze to hydroxamic acids, HA, which are well-known complexing agents of many metal ions, including ^{95}Zr. The formation of very stable HA–^{95}Zr complexes has been proposed as a rationale for the retention of ^{95}Zr in the diluents. However, the results of this study carried out in a model system, the acid-catalyzed conversion of 1-nitropropane to propanhydroxamic acid, and the subsequent hydrolysis to carboxylic acid and hydroxylamine—easily extensible to the actual reprocessing processes—indicate that in these systems the equilibrium concentration of hydroxamic acids attainable is too low (10^{-8} to 10^{-9} M) to account for the "zirconium retention" phenomenon.

INTRODUCTION

The mixture of high molecular weight paraffins used as the diluent of tri-*n*-butylphosphate (TBP) in the selective extraction procedures during the reprocessing of the irradiated nuclear fuels undergoes both radiolytic and chemical degradation, the latter caused by contact with the aqueous solution of nitric acid (*1*). The degradation compounds formed are considered to be responsible for the retention in the organic phase of some fission products, in particular ^{95}Zr–^{95}Nb, which cannot be removed by ordinary procedures (*1, 2*). As a consequence, an undesirable increase of the residual radioactivity of the diluent builds up. A reasonable possibility (*1, 2*) is that such degradation products behave as effective ligands of zirconium, giving rise to very stable complexes in the organic phase. However, the nature of such complexing species is still a matter of debate in spite of the large number of studies concerned with this particular aspect. In fact, some hypotheses have been advanced, and among them the most favored implies the formation in the two-phase system of hydroxamic acids, HA (*1, 3*). Indeed, HA, which may be obtained from primary nitroalkanes (*1, 4*), are very good complexing agents of Zr as well as of many other metal ions (5). On the other hand, any attempt to detect them in the diluents has so far failed. This circumstance does not allow dismissal of the hypothesis since even very minute amounts of HA (10^{-6} *M*, almost at the limit of the available analytical techniques) may cause "zirconium retention." Some new explanations have recently been offered for the phenomenon. Thus the zirconium retention has been rationalized as arising from the occurrence of lipophilic inorganic forms of the metal (*6*). Alternatively, the complexing agent has been postulated to be the butyl lauryl phosphoric acid originated from the radiolysis of TBP and dodecane (*7*).

Neither explanation is completely convincing, and it is likely that zirconium retention originates from several mechanisms.

In this work we have tested the "hydroxamic acids theory" in the hope of finding some clear-cut evidence in favor or against their involvement.

Since the direct determination of very low concentrations of HA appears to be a very difficult task, we decided to approach this problem from a completely different point of view. It is known that, as mentioned above, the nitration of paraffins also produces, among various nitro derivatives, primary nitroalkanes (*8*) which hydrolyze in acid solution to HA (*4*). In turn, these are again converted in acidic medium to carboxylic acids and hydroxylamine (*4d, 9*) Thus, by measuring under the same conditions both the rate of formation of an hydroxamic acid from the primary nitroalkane and that of the transformation to carboxylic acid, one should be able to evaluate the theoretical concentration for a given "stationary" concentration of nitroalkane.

This measurement has been made in a model system, as discussed below. The information collected, which is reported in this paper, has been extended to the actual reprocessing systems. It may be anticipated that, on the basis of this study, it is very unlikely that the concentration of HA in the diluent may reach a level high enough to account for the "zirconium retention" phenomenon.

EXPERIMENTAL

Materials

All water used in the experiments was doubly distilled. Reagent grade 1-nitropropane, propionic acid, hydroxylamine, $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3$, $NaNO_2$, and concentrated (96%) sulfuric acid were used without further purification. HNO_3 (65%), reagent grade, was purified from nitrous vapors by bubbling nitrogen gas for 24 h before use. Propanhydroxamic acid was prepared by reacting ethylpropionate with hydroxylamine according to a reported procedure (*21*).

Kinetics

Rate constants for 1-nitropropane (NP) hydrolysis at 70, 81, and 90°C in H_2SO_4 solution were determined by using two different techniques. In the spectrophotometric method the progress of the reaction is followed by monitoring the disappearance of the absorbance of NP at 271 nm ($\varepsilon = 23$); in a typical example, 50 μL of NP was added to a solution of H_2SO_4 (25 mL) of the required concentration in a stoppered flask immersed in a thermostatic bath. The temperature control was better than ±0.3°C. Aliquotes (2 mL) of the reaction mixture were withdrawn at regular time intervals and maintained at 25°C for 10 min before measuring the absorbance using a Gilford Model 2400 spectrophotometer. Rate constants were evaluated from the slopes of plots of log $(A - A_\infty)$ vs time. A_∞ is usually negligible. The plots were linear to greater than 3 half-lives. The reproducibility was within ±3–5%.

The rate constants for the hydrolysis of NP were also determined by following the increase of hydroxylamine concentration as measured by titration with bromate ion (*4c*). In a typical example, 0.4 mL of NP was added to a solution of H_2SO_4 (50 mL) of the required concentration in a stoppered flask in a thermostatic bath. The temperature control was better than ±0.2°C. Aliquots (3 mL) of this solution were withdrawn at regular time intervals and added to a solution of 0.1 N $KBrO_3$ (20 mL) and 5 N HCl (20 mL). After 15 min an excess of KI (15% w/v aqueous solution) was added and the iodine formed was quantitatively analyzed by titration with $S_2O_3^{2-}$ according to the standard procedure (*20*). Rate constants were evaluated from the slopes of plots of log [hydroxylamine] vs time, which are linear to greater than 2 half-lives. The reproducibility was within ±5–7%.

The progress of the hydrolysis of PHA in H_2SO_4 solution at 25, 35, and 45°C was followed spectrophotometrically by monitoring the disappearance of the absorbance of PHA at 221 nm ($\varepsilon = 235$ in 7.31 N H_2SO_4). In a typical experiment, 100 mL of a 0.1 M aqueous solution of PHA was mixed with a solution of H_2SO_4 (2 mL) of the required concentration directly in a quartz cell placed in the thermostated cell compartment of the spectrophotometer. The temperature control was better than ±0.2°C. Rate constants were evaluated from the slopes of plots of log $(A - A_\infty)$ vs time. A_∞ is usually negligible. The plots were linear to greater than 3 half-lives. The reproducibility was within ±2–3%.

For reactions in the presence of $FeCl_3 \cdot 6H_2O$, the disappearance of PHA was monitored at 503 nm, a wavelength corresponding to the adsorption of the complex PHA–Fe(III) (*7*).

The rate constants of the hydrolysis of PHA in HNO_3, both in the absence and in the presence of $NaNO_2$, were evaluated by withdrawing aliquots of the reaction mixture at regular time intervals. These were added to a solution of $Fe(NO_3)_3$. Thus the absorbance at 503 nm was measured. In all cases when the disappearance of PHA was observed at 503 nm [PHA–Fe(III) complex], the plots of log $(A - A_\infty)$ vs time were linear to greater than 2 half-lives. The reproducibility was within ±3–5%.

The activation energies were evaluated by means of (*23*)

$$\log k = \cos t + E_A/4.576T \qquad (14)$$

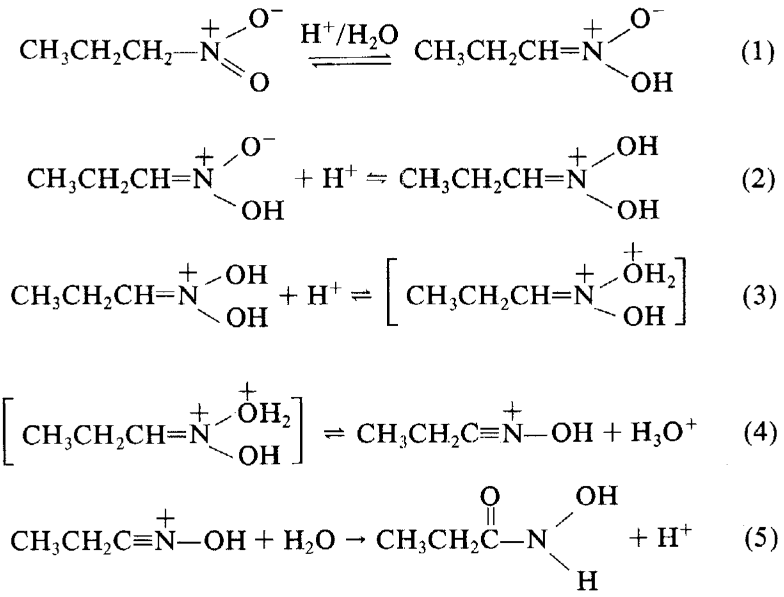
A good linearity ($r > 0.99$) of plots of log k vs $1/T$ was observed in all cases.

RESULTS AND DISCUSSION

The reaction studied in this work is the hydrolysis of NP in aqueous sulfuric acid. It is clear that this very simple model system differs in many respects from the actual ones. Thus NP is fairly soluble in water whereas the nitroalkanes formed by nitration of the diluents are much more hydrophobic owing to their much longer carbon chain. Accordingly, the hydrolysis of NP is carried out in aqueous solution instead of in a two-phase system. Furthermore, the acid catalysis is provided by added sulfuric acid, whereas in the reprocessing procedures the aqueous phase is a solution of nitric acid containing nitrous compounds together with a variety of metal ions. Nevertheless, we will show that the results obtained with our simplified model are very useful, allowing one to draw a conclusion of general validity.

Hydrolysis of 1-Nitropropane (NP)

NP is hydrolyzed under acid catalysis to propanhydroxamic acid, PHA. The mechanism of the reaction is not known with certainty, but Scheme 1 proposed by Kornblum (*10*), appears to be a likely pathway.

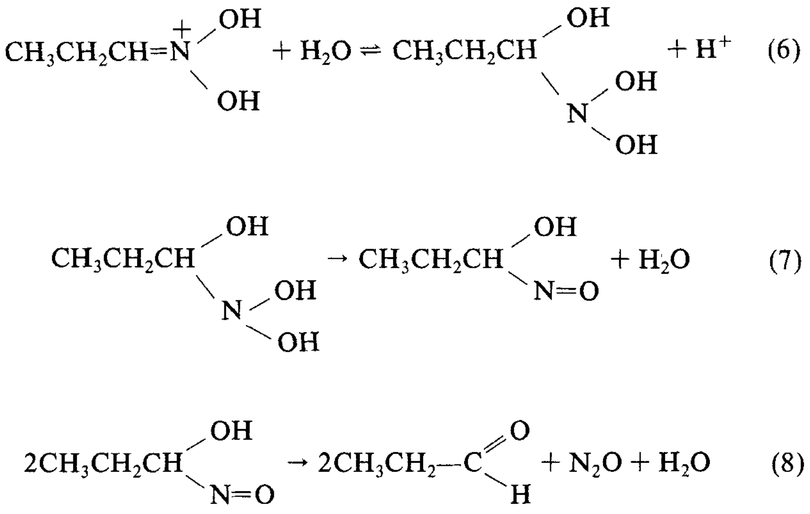


SCHEME 1.

It should be noted that Scheme 1 suggests the intermediacy of the *aci* form of the nitroalkane, Eq. (1), which is protonated in two subsequent steps, Eqs. (2) and (3), before the elimination of the molecule of water, Eq. (4). Therefore, the possibility exists that the reaction proceeds through a different pathway, the Nef reaction [10, 11], which leads to the formation of propionaldehyde according to Scheme 2.

Comparison of the two schemes indicates that the Nef reaction should be favored at low acidities, as it involves the loss of a proton from the protonated *aci* form, Eq. (6), whereas the formation of PHA, which requires further protonation, Eq. (3), should predominate at higher acidity.

In order to ascertain the relative relevance of the two possible routes of disappearance of NP, we have measured the rate of hydrolysis by means of



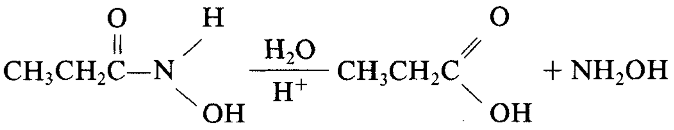
$$CH_3CH_2CH{=}\overset{+}{N}(OH)_2 + H_2O \rightleftharpoons CH_3CH_2CH(OH)N(OH)_2 + H^+ \qquad (6)$$

$$CH_3CH_2CH(OH)N(OH)_2 \rightarrow CH_3CH_2CH(OH)N{=}O + H_2O \qquad (7)$$

$$2CH_3CH_2CH(OH)N{=}O \rightarrow 2CH_3CH_2{-}C({=}O)H + N_2O + H_2O \qquad (8)$$

SCHEME 2.

two different techniques. Thus the disappearance of NP has been monitored by following the decrease of the absorbance at 271 nm, a wavelength where none of the possible products shows an appreciable absorption; at 81.5 ± 1.5°C, a temperature at which the reaction proceeds conveniently fast; and at various sulfuric acid concentrations measured either as percentage of H_2SO_4 or as H_0. [The acidity function H_0 (*12*) has been used as a convenient measure of the acidity of the medium. It does not have any implication under a mechanistic point of view (*13*).] At the same time, since it is well known that PHA, in acid solution, is further hydrolyzed to propionic acid, PA, and hydroxylamine, as in



$$CH_3CH_2C({=}O){-}N(H)OH \xrightarrow[H^+]{H_2O} CH_3CH_2C({=}O)OH + NH_2OH \qquad (9)$$

we have measured the rate of formation of hydroxylamine by means of a titrimetric technique (see Experimental) (*4c*). The results of this study are collected in Table 1 in terms of first-order rate constants and graphically shown in Fig. 1 for the experiments at 81°C. Linear plots of log [NP] or log $[NH_2OH]$ vs time are obtained with both techniques.

The very good agreement of the rate constants obtained by the two different techniques, even at relatively low acidity, indicates that the contri-

TABLE 1

Rates of Hydrolysis of 1-Nitropropane (9 × 10^{-2} M) at Various Acid (H_2SO_4) Concentrations in Water

H_2SO_4 (%)	H_0[a]	t (°C)	10 k_{obs}^{NP}[b] (s^{-1})
8.25	−0.18	70	2.9
14	−0.58	70	2.8
46	−2.70	70	0.67
82	−6.87	70	21.8
8.25	−0.17	81	7.5
10	−0.29	81	9.4[c]
14	−0.57	81	8.3
18	−0.82	81	10.4[c]
25	−1.26	81	8.2[c]
39	−2.13	81	3.1[c]
46	−2.67	81	2.6
59	−3.78	81	2.2[c]
66	−4.54	81	6.1
74	−5.61	81	19.0
76	−5.88	81	23.3[c]
82	−6.73	81	74.5
8.25	−0.14	90	15.2
14	−0.51	90	14.2
46	−2.55	90	6.2
82	−6.42	90	171.4

[a] Data from Ref. *14*.

[b] Determined from pseudo-first-order integrated plots using the titrimetric technique (see Experimental).

[c] Pseudo-first-order rate constants obtained by the spectrophotometric technique (see Experimental).

bution of the Nef reaction to the overall rate of disappearance of NP is negligible, i.e., in the range of acid concentrations explored, the nitroalkane is quantitatively converted to hydroxamic acid and no aldehyde is formed.

The shape of the curve of Fig. 1 clearly suggests a complex dependence of the rates of hydrolysis of NP on the acidity of the medium, as could have been predicted on the basis of the multistep mechanism of Scheme 1.

However, the analysis of the other elemental reactions which lead to the formation of PHA is outside the aim of the present study.

Also collected in Table 1 are the rate constants of NP hydrolysis at 70 and 90°C at four different sulfuric acid concentrations corresponding to the apparently different reaction paths indicated by Fig. 1. These data allow the evaluation of the activation parameters which are reported in Table 2. It may

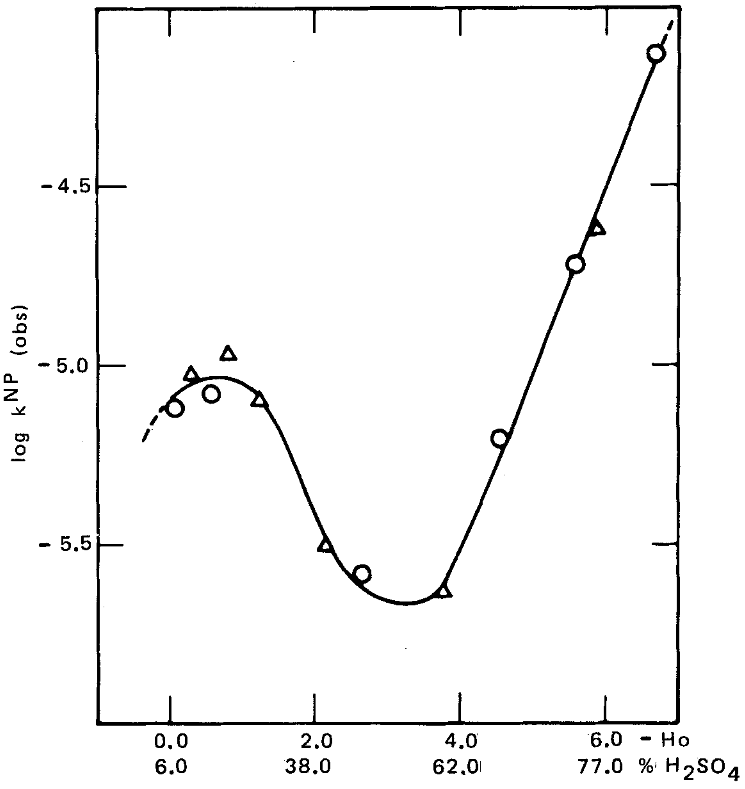


FIG. 1. Variation of the first-order rate constants for the hydrolysis of 1-nitropropane with the acidity (H_2SO_4) in water at 81°C.

TABLE 2

Activation Energies for the Hydrolysis of 1-Nitropropane Calculated from the Data in Table 1

H_2SO_4 (%)	E_A[a] (kcal/mol)
8.25	20.9 ± 0.5
14.0	20.5 ± 0.5
46.0	27.9 ± 0.5
82.0	25.8 ± 0.6

[a] Determined from the slope of linear plots of log k_{obs}^{NP} vs $1/T$.

also be seen that the activation energies vary with the concentration of sulfuric acid, thus confirming that the various processes involved in the overall reaction are differently affected by the acidity of the medium. The determination of the activation parameters of the hydrolysis of NP will allow, as discussed below, calculation of the rate constants at lower temperatures so that a comparison with the rate of hydrolysis of PHA to PA can be made. In fact, owing to the large difference in the values of the rate constants, the two reactions have to be carried out in different temperature ranges.

Hydrolysis of Propanhydroxamic Acid (PHA)

The rate of disappearance of PHA has been measured by following the decrease of the absorbance at 221 nm. At this wavelength neither product of the reaction, propionic acid or hydroxylamine, shows appreciable absorption.

Thus linear plots of $\log A_{221}$ vs time are obtained which provide the value of the first-order rate constant as the slope. The reaction has been investigated at three temperatures, 25, 35, and 45°C, in a wide range of acid concentrations. The pertinent rate constants are reported in Table 3. Also, the variation of the rates with acidity at 25°C is reported in Fig. 2 as an example. It may be observed that the dependence of the hydrolysis of PHA on the acid concentration is also rather complex, somewhat resembling that observed in the acid-catalyzed hydrolysis of esters and amides (*15*). In fact, the rates pass through a maximum at different acid concentrations depending on the temperature. The bell-shaped profile observed might suggest, by analogy with the previously mentioned reactions of carboxylic acid derivatives (*15, 16*), that a water molecule is involved in the rate-determining step. This mechanistic aspect has not been further investigated. In Table 3 a comparison is also made between the effect of sulfuric and nitric acid on the hydrolysis rates. Provided that the acid strength of the medium, measured as H_0, is the same, the two acids exert an identical catalytic effect within experimental errors. This is not at all surprising considering that the acidity of the medium, rather than the nature of the acid, is the factor which plays a role in acid-catalyzed hydrolysis. The data of Table 3 allow the determination of the activation parameters of the hydrolysis of PHA at four different acid concentrations as reported in Table 4. From these parameters the values of the rate constants can be calculated for higher temperatures which are closer to those employed in the hydrolysis of NP, corresponding to those normally measured during the reprocessing procedures.

TABLE 3

Rates of Hydrolysis of Propanhydroxamic Acid[a] at Various Acid Concentrations in Water

Acid			t	$10^5 k_{\text{obs}}^{HA\,c}$
Type	%	$H_0{}^b$	(°C)	(s^{-1})
H_2SO_4	9.5	−0.31	25	3.8
	17.5	−0.88	25	6.9
	24	−1.34	25	9.1
	33	−1.92	25	9.7
	37.5	−2.24	25	9.2
	42.5	−2.64	25	6.8
	48.5	−3.16	25	3.5
	57.2	−4.04	25	1.8
	74	−6.47	25	0.07
HNO_3	12	−0.67[d]	25	5.8
	17.6	−1.04[d]	25	8.2
	22.4	−1.33[d]	25	8.9
H_2SO_4	9.5	−0.29	35	9.0
	33	−1.88	35	22.2
	42.5	−2.58	35	18.5
	57.2	−3.94	35	4.0
	9.5	−0.26	35	20.0
	33	−1.83	35	50.0
	42.5	−2.52	35	39.6
	57.2	−3.83	35	10.5

[a] The initial concentration of PHA was 1 to 3.5×10^{-3} *M*.

[b] See footnote *a*, Table 1.

[c] Determined from pseudo-first-order integrated plots using the titrimetric technique (see Experimental).

[d] Data from Ref. *17*.

TABLE 4

Activation Energies for the Hydrolysis of Propanhydroxamic Acid, Calculated from the Date in Table 3

H_2SO_4 (%)	$E_A{}^a$ (kcal/mol)
9.5	15.7 ± 0.4
33	15.6 ± 0.4
42.5	16.7 ± 0.4
57.2	17.0 ± 0.4

[a] Determined from the slope of linear plots of $\log k_{\text{obs}}^{\text{HA}}$ vs $1/T$.

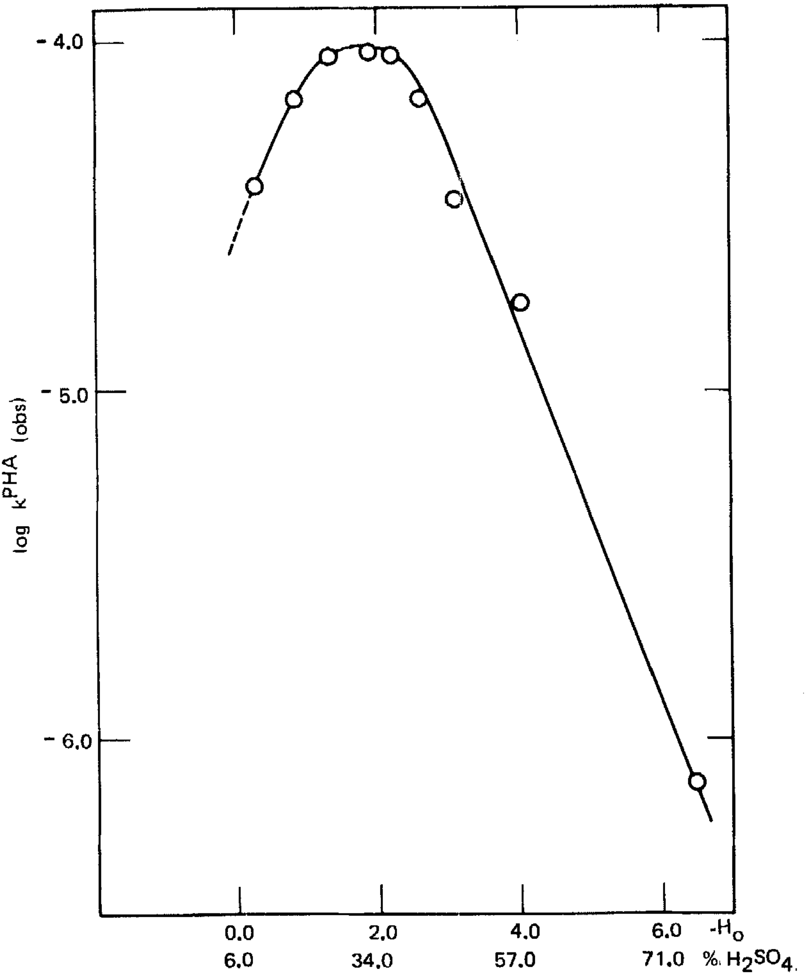


FIG. 2. Variation of the first-order rate constants for the hydrolysis of propanhydroxamic acid with the acidity (H_2SO_4) in water at 25°C.

TABLE 5

Effect of the Addition of $FeCl_3 \cdot 6H_2O$ (2.3×10^{-2} *M*) on the Rates of Hydrolysis of Propanhydroxamic Acid (8×10^{-3} *M*) at Various Acid (H_2SO_4) Concentrations in Water at 25.00°C

H_2SO_4 (%)	$H_0{}^a$	$10^5 k_{obs}^{HA\,b}$ (s^{-1})
10	−0.35	3.2 (4.1)
25	−1.40	7.4 (9.2)
34	−1.99	7.5 (9.6)
39.5	−2.38	6.8 (8.3)
44	−2.77	4.8 (6.2)

[a] See footnote *a*, Table 1.

[b] Determined from pseudo-first-order integrated plots using the spectrophotometric technique [disappearance of the absorbance at 503 nm of the complex Fe(III)–PHA] reported in Experimental. Values in parentheses are the rate constants in the absence of Fe(III) obtained by interpolation of the data of Table 3.

The effect on the hydrolysis of PHA in the presence of some additives which are very likely to be found in the actual reprocessing systems has been briefly investigated. Therefore, as reported in Table 5, a fixed amount of Fe(III) has been added to the reaction mixture at various acidities. The rate constants thus measured by following the disappearance of the absorbance at 503 nm, the typical absorption band of the complex Fe(III)–PHA (*9*), indicate a very modest retardation effect by added Fe(III). This may be taken as evidence that the coordination of PHA to a metal center does not significantly affect its reactivity toward hydrolysis. On the contrary, the data of Table 6 show that a dramatic enhancement of the rate of disappearance of PHA is observed when nitrous acid, added as $NaNO_2$, is present in solution, probably because of the nitrosation of PHA (18) which proceeds apparently much faster than its hydrolysis.

Estimation of the Maximum Concentration of PHA

Our model system, which has been selected to be as simple as possible, consists of two first-order consecutive reactions:

$$\mathrm{NP} \xrightarrow{k_1} \mathrm{PHA} \qquad (10)$$

TABLE 6

Effect of the Addition of $NaNO_2$ on the Rates of Hydrolysis of Propanhydroxamic acid (2.6×10^{-2} M) in aqueous HNO_3 ($4M$) at 25.00°C

$10^2[NaNO_2]$ (M)	$t^{1/2}$ (min)
None	138
2.0	~1
2.7	Too fast

$$\mathrm{PHA} \xrightarrow{k_2} \mathrm{PA} + \mathrm{NH_2OH} \tag{11}$$

It may be shown that the maximum equilibrium concentration of propanhydroxamic acid, $[\mathrm{PHA}]_{\max}$, is given by (*19*)

$$[\mathrm{PHA}]_{\max} = \beta_{\max}[\mathrm{NP}]_0 \tag{12}$$

where $[\mathrm{NP}]_0$ indicates the initial concentration of 1-nitropropane and $\beta_{\max}$ is defined as

$$\beta_{\max} = K^{K/(1-K)} \tag{13}$$

where $K = k_2/k_1$. Therefore the evaluation of [PHA], once $[\mathrm{NP}]_0$ is known, simply requires the calculation of the $\beta_{\max}$ value. This, in turn, is easily obtained from the values of k_1 and k_2, i.e., the rate constants for the two reaction studied, which are available at any desired temperature by using the activation parameters of the reactions. Accordingly, the values of $\beta_{\max}$ have been calculated at three temperatures, 40, 50, and 60°C, at many acid concentrations to obtain the curves of Fig. 3. The three curves have a minimum of $[\mathrm{PHA}]_{\max}$ (Eq. 12), slightly dependent on the temperature at an acidity range not far from that normally employed in the aqueous phase of the reprocessing systems. For example, assuming $[\mathrm{NP}]_0 = 1$ M, in this acidity region the $[\mathrm{PHA}]_{\max}$ is $\sim 1 \times 10^{-4}$ M. The treatment described above is subject to a direct check. In fact, at the highest acid concentrations, where the rate of hydrolysis of PHA is very slow and that of its formation from NP is very fast, one may add known amounts of NP and by employing a standard analytical technique (*9*) (see Experimental), measure the concentration of PHA. The value thus obtained agrees particularly well with the one calculated on the basis of Eq. (12). In Fig. 4 an example is reported of a

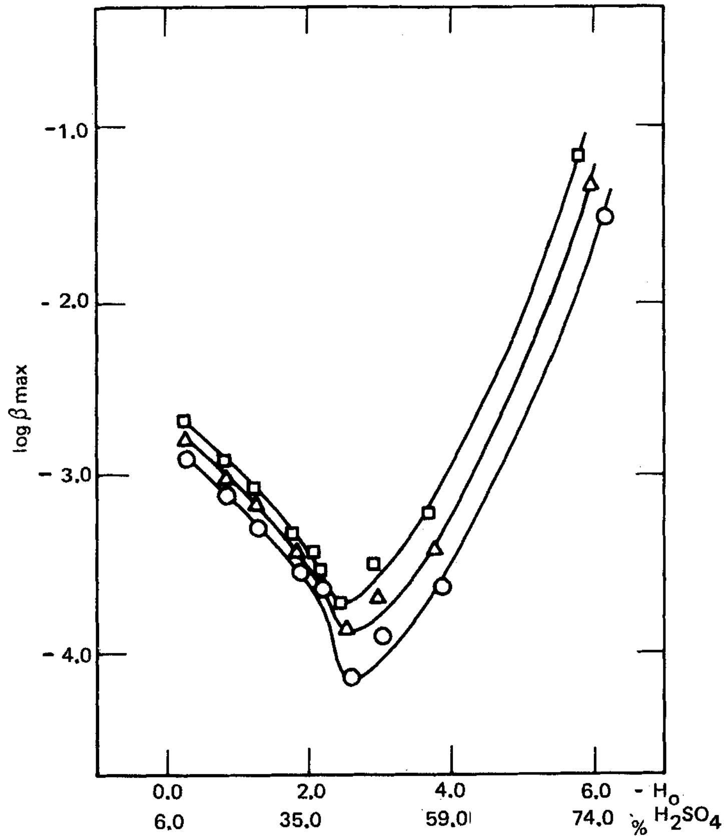


FIG. 3. Variation of β_{max} (see text) with the acidity (H_2SO_4) in water at 40°C (○) 50°C (△) and 60°C (□).

kinetic run which demonstrates this point. Unfortunately, this check cannot be made at lower acidities due to the fast hydrolysis of PHA. However, there is little reason to doubt that Eq. (12) is valid in the entire range of acid concentrations investigated.

Once β_{max} values are available, the initial concentration of nitroalkane must be known to obtain the maximum concentration of PHA. This is an important point as far as the extension of this kind of treatment to real systems is concerned. Therefore, some assumptions should be made, and these are discussed in the next section.

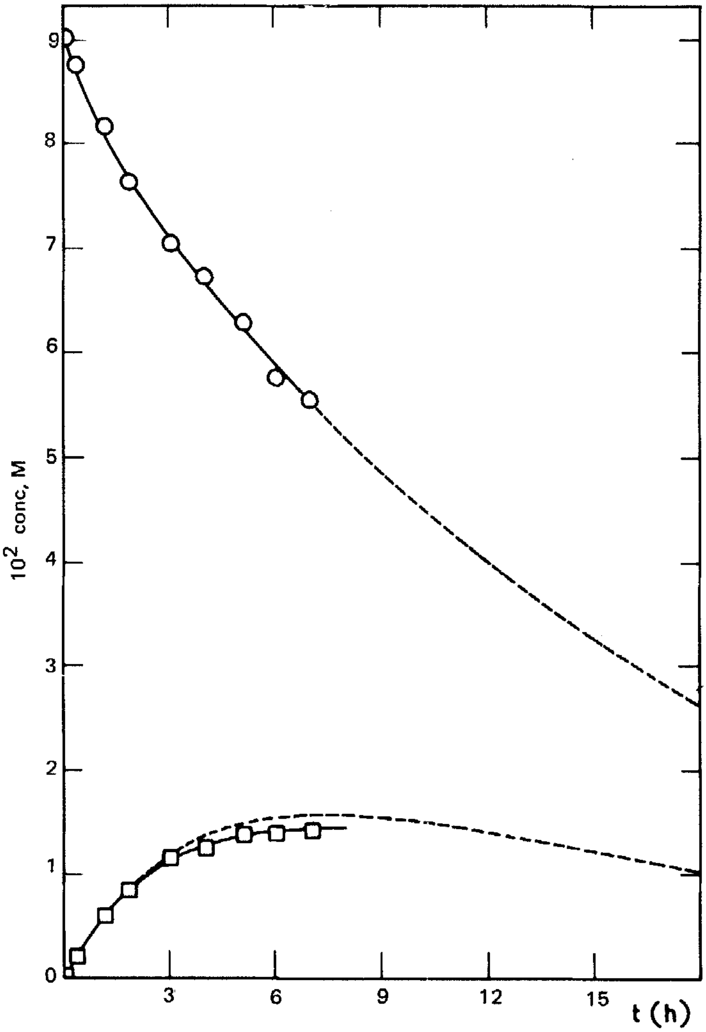


FIG. 4. Decrease of the concentration of 1-nitropropane (○) and increase of the concentration of propanhydroxamic acid (□) with time in 74% H_2SO_4 at 81°C. Dotted lines are calculated on the basis of the rate constant value for the hydrolysis of NP and according to Eq. (12) (see text), respectively.

Estimation of the Equilibrium Concentration of PHA in the Diluents

Contact of the solution of HNO_3 with the diluent in a two-phase system is not likely to produce an amoung of nitro compounds larger than 10% of the total hydrocarbon. However, let us take this figure, which is overestimated, and therefore assigning the pariffins an average molecular weight of ~200, assume a concentration of nitro compounds of about 0.5 *M*.

The portion of primary nitroalkanes, which are the sole precursors of HA, cannot be more than 1% of the total nitro compounds [20] and consequently the concentration of primary nitroalkanes is reduced to 5×10^{-3} *M*. It is reasonable to assume that this is a "stationary" concentration i.e., that an equilibrium is established in which the rate of formation of primary nitroalkanes equals that of their consumption through the hydrolytic processes discussed previously. However, it is worth mentioning that the hydrolysis must proceed in the aqueous phase and therefore a partition of the nitro derivative between the two phases should be envisaged.

The same possibility exists for the hydroxamic acids formed in the aqueous phase. Taking into account this situation, one might wonder whether the treatment of the data on the basis of the $\beta_{\max}$ values obtained in the previous section is still valid. However, it is easily shown that in a two-phase system, by employing the partition coefficients, an equation very similar to Eq. (12) may be used. For the model compounds studied, it is

$$[\mathrm{PHA}]_{\max}^{\mathrm{OR}} = \beta_{\max}\,[\mathrm{NP}]_{\max}^{\mathrm{OR}}\frac{K_2}{K_1} \tag{14}$$

where $[\mathrm{PHA}]_{\max}^{\mathrm{OR}}$ and $[\mathrm{NP}]_{\max}^{\mathrm{OR}}$ are the concentrations in the organic phase and K_1 and K_2 are the partition coefficients of NP and PHA, respectively. For the two model substrates, as well as for the compounds formed in the reprocessing, it is expected that the value of the ratio K_2/K_1 will be less than 1, owing to the intrinsically greater hydrophilicity of the hydroxamic group as compared with that of the nitro group. Therefore, the use of the $\beta_{\max}$ values previously determined may only result in an overestimation of the concentration of HA in the organic phase. A further reasonable assumption which should be made for using the $\beta_{\max}$ values is that the reactivity toward hydrolysis of the model compounds is similar to that of the corresponding products formed in the real systems, i.e., and k_1 and k_2 used for calculating the $\beta_{\max}$ values, or better, the ratio k_2/k_1, does not significantly depend on the carbon chain.

According to Eq. (12), for a $\beta_{\max}$ value of 1.4×10^{-4} at 50°C and $H_0 = -2.54$, close to the minimum of Fig. 3, for a "stationary" concentration of primary nitroalkanes of 5×10^{-3} *M*, the calculated concentration of hydroxamic acids is 7×10^{-7} *M*.

This figure, which is already very small, is overestimated not only because of the assumption made before—10% nitration of the diluent and K_2/K_1 assumed to be 1—but also because nitrous acid is always present in the solution of nitric acid used in the reprocessing. On the basis of the data collected in this paper, nitrous acid is believed to lower the equilibrium concentrations of hydroxamic acids by at least two powers of ten by enhancing the rate of their decomposition. This leads to an estimated concentration of hydroxamic acids as low as $\sim 10^{-8}$ to 10^{-9} M.

In conclusion, even though HA are extremely good ligands for zirconium, their concentration in the diluents should be much too small for explaining the "zirconium retention" phenomenon which therefore is probably due to other complexing agents or, more likely, to the concurrence of several different factors.

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