

THE PROPERTIES OF PROTACTINIUM(V) IN ALKALINE SOLUTIONS

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In a preliminary note¹ we have reported that a soluble form of Pa(V) may be obtained by fusing ²³³Pa tracer in NaOH and diluting with water. In such solutions Pa(V) was shown to move on filter paper when developed with *N* KOH and to migrate slowly toward the anode in paper electrophoresis with *N* KOH as electrolyte.

In this paper we wish to describe further work on the behaviour of Pa(V) in alkaline solutions.

EXPERIMENTAL

I. The preparation of solutions of Pa(V) in alkali

²³³Pa tracer in 6 *N* HCl was evaporated in a microbeaker, a few pellets of NaOH or KOH were added and fused over a naked flame for a few minutes, cooled and diluted with water to yield a solution 5 *N* with respect to alkali. Such solutions usually contain a soluble fraction but also an insoluble activity. If the solution in HCl is taken to dryness and moistened with conc. HCl and again evaporated and this process repeated three times the insoluble compound does not form. It seems that during evaporation with 6 *N* HCl some radiocolloid is formed which does not react readily with NaOH. When evaporated repeatedly with conc. HCl this seems to be inhibited and presumably the Pa(V) is left in the beaker as a very thin layer on the surface which then reacts readily with fused NaOH.

When solutions which have been evaporated three times with conc. HCl are treated with aqueous 6 *N* KOH some transformation into a soluble form was also noted. Without this pretreatment as reported previously¹ no soluble fraction is obtained.

II. Paper chromatography

Our first evidence for the solubility of Pa(V) was found by chromatographing solutions prepared as in (I) on Whatman No. 1 paper (unwashed) with *N* NaOH or *N* KOH as solvent. The Pa(V) has here an R_F value of about 0.5. We then tried to obtain evidence on the mode of adsorption and stability of the protactinate ion by chromatographing with various concentrations of NaOH and KOH. However, no consistent results could be obtained further than that Pa(V) remains soluble under various conditions.

The studies with anion exchange resins (described below) then indicated that the Pa is present as a polyvalent anion. In this case the impurities of the paper (Ca, Mg,

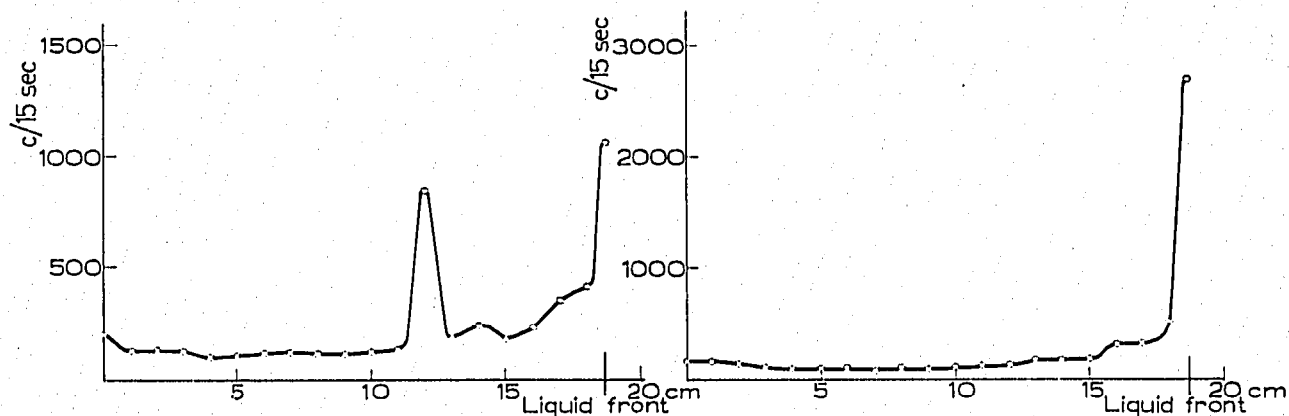


Fig. 1

Fig. 2

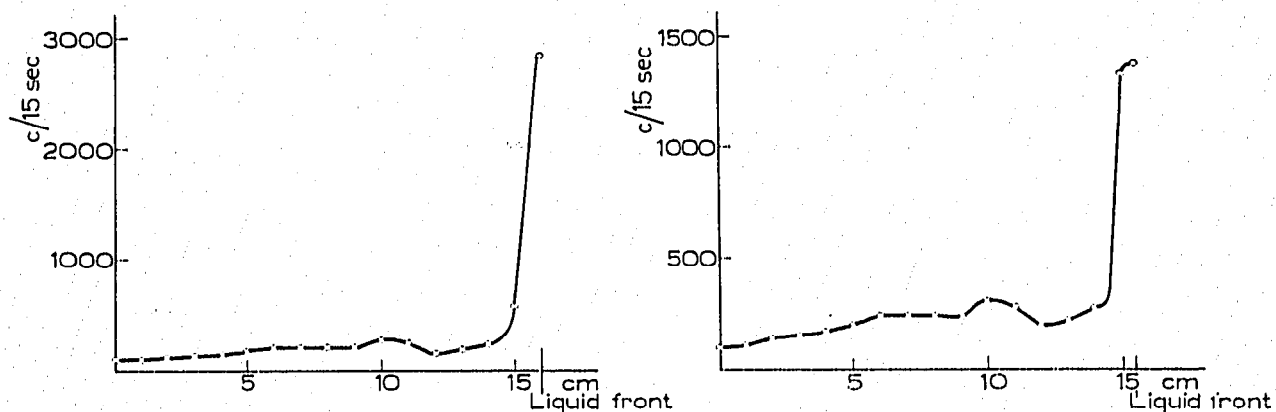


Fig. 3

Fig. 4

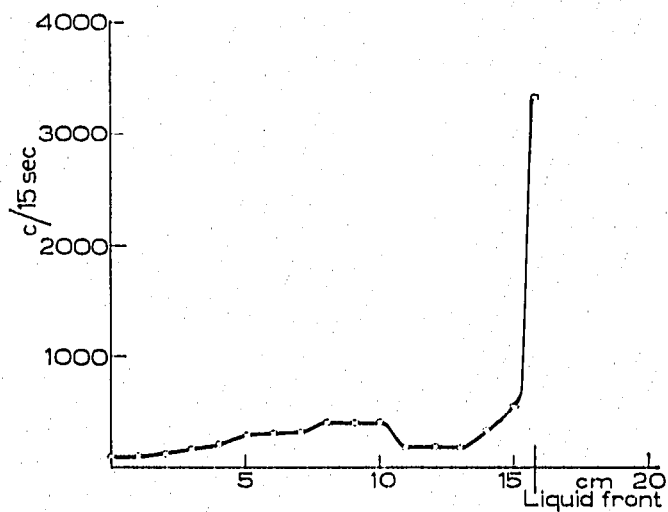


Fig. 5

Figs. 1-5. Paper chromatograms of protactinate developed on washed Whatman No. 1 paper with: (1) 0.1 *N* KOH. (2) 0.5 *N* KOH. (3) 1 *N* KOH. (4) 2 *N* KOH. (5) 3 *N* KOH.

Fe and Cu) would have to be removed by washing with HCl and water to prevent precipitation of the protactinate or a complexing agent such as ethylenediaminetetraacetic acid (EDTA) added to complex these impurities.

Chromatograms on washed paper are shown in Figs. 1-5. The protactinate moves with the liquid front and not as on unwashed paper with an R_F 0.5 and is stable down to 0.1 N KOH, the lowest concentration of alkali tried as developer. In 0.1 N KOH two peaks of activity are however formed. On unwashed paper with alkali solutions containing 1% EDTA the elution is not as complete. In 2 N KOH most of the Pa moves rather fast but in lower concentrations appreciable amounts stay at the start. Thus EDTA does not complex all metals efficiently at lower concentrations of KOH.

III. Anion exchange of protactinate

Protactinate solutions in KOH from 0.2 to 2 N were equilibrated with weighed amounts of Dowex-2. Good results are only obtained when all solutions are freshly prepared and kept in stoppered bottles as absorption of CO_2 from the atmosphere

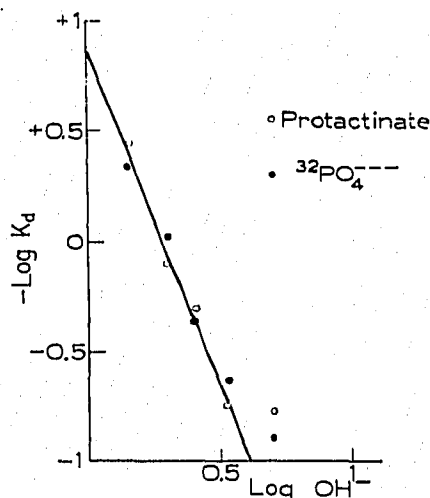


Fig. 6. Anion exchange adsorption of protactinate and tracer $^{32}\text{PO}_4^{--}$ in KOH of varying concentrations. $-\log K_d$ is plotted against $\log \text{OH}^-$ of the solution.

may alter the equilibria considerably. 1 g lots of Dowex-2 were converted to the OH form by washing three times with 2 N KOH and three times with distilled water. The solution of protactinate in the required concentration of KOH was then added and shaken for two hours to reach equilibrium, a portion withdrawn and its activity determined, and the amount adsorbed calculated from the loss of activity. The equilibrium constant K_d was then calculated and its logarithm plotted against $\log \text{OH}^-$ as shown in Fig. 6.

$$K_d = \frac{\text{amount adsorbed}}{\text{amount in solution}} \times \frac{\text{volume of solution}}{\text{mass of resin}}$$

In this equilibrium between OH^- , a monovalent ion, and protactinate the tangent of the line obtained when $\log K_d$ is plotted against $\log \text{OH}^-$ should indicate the valency of the protactinate ion. The tangent in Fig. 6 is 3.1 thus indicating that the protac-

tinate, if present as a single anion and not a mixture of several anions of different valencies, would have a valency of three. In order to check our experimental method and calculations we also carried out identical equilibrium experiments with tracer $^{32}\text{PO}_4^{-3}$. As also shown on Fig. 6, phosphate gives results identical to protactinate.

IV. Adsorption on glass

In order to prevent an error due to adsorption on the walls of the test tubes used in the above ion-exchange experiments, a "blank" experiment, *i.e.* one without the resin, was carried out for each concentration of KOH. The adsorption on glass was found to be negligible and below the accuracy of our activity measurements.

V. Solvent extraction

Solutions of protactinate in *N*, *2 N* and *3 N* KOH were shaken with equal volumes of butanol and methyl propyl ketone. The partition coefficients were determined by measuring the activity in both the aqueous and the solvent phase. Table I shows that the amount extracted is very small in all cases.

TABLE I
SOLVENT EXTRACTION OF PROTACTINATE

Normality of KOH	Solvent	% extracted (approximate)
1	Butanol	2
2	Butanol	5
3	Butanol	5
1	Methyl propyl ketone	7
2	Methyl propyl ketone	4
3	Methyl propyl ketone	4

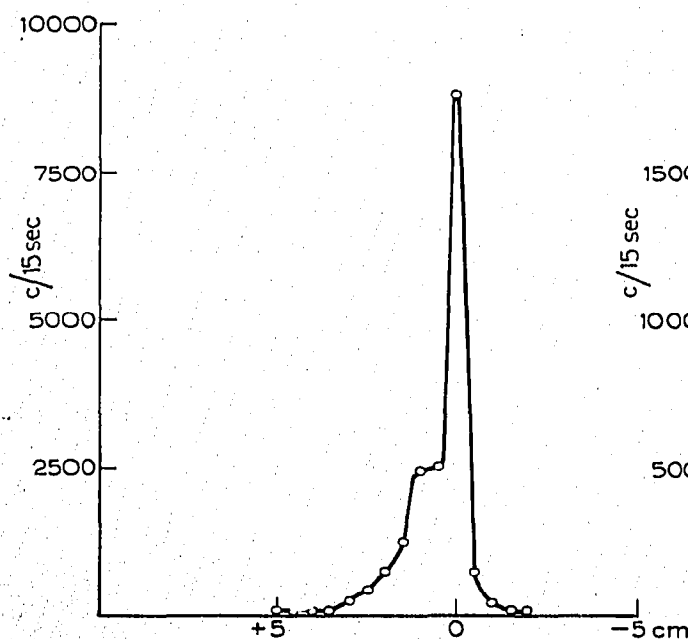


Fig. 7

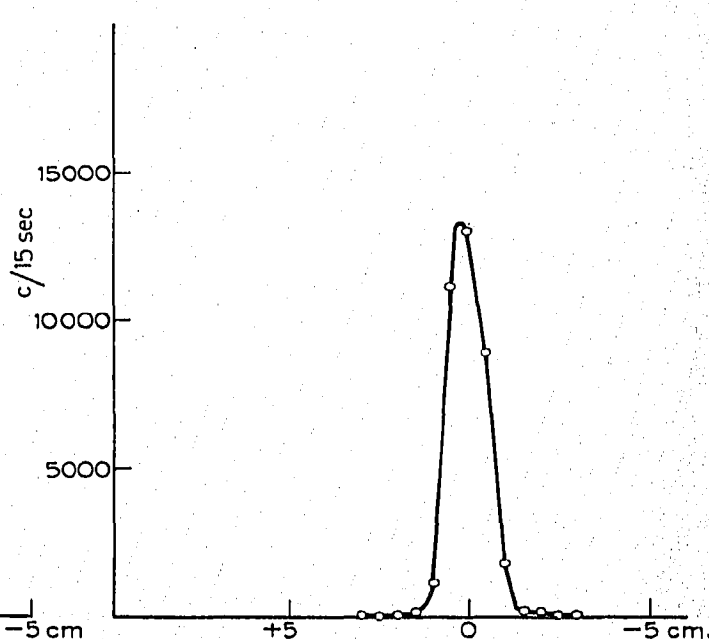


Fig. 8

VI. Precipitation with metal ions

In our paper chromatographic work we have reported that the retention of protactinate was due to metal impurities in the filter paper. We thus devised a simple method for determining when protactinate is precipitated or coprecipitated, by placing a drop

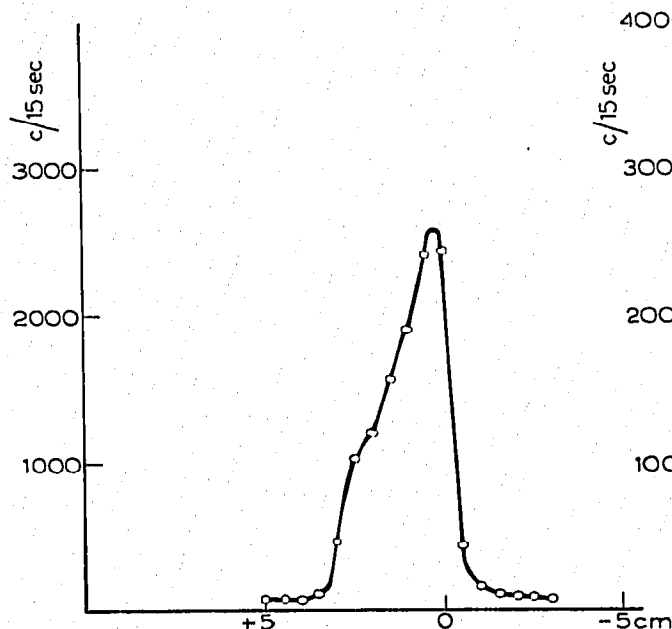


Fig. 9

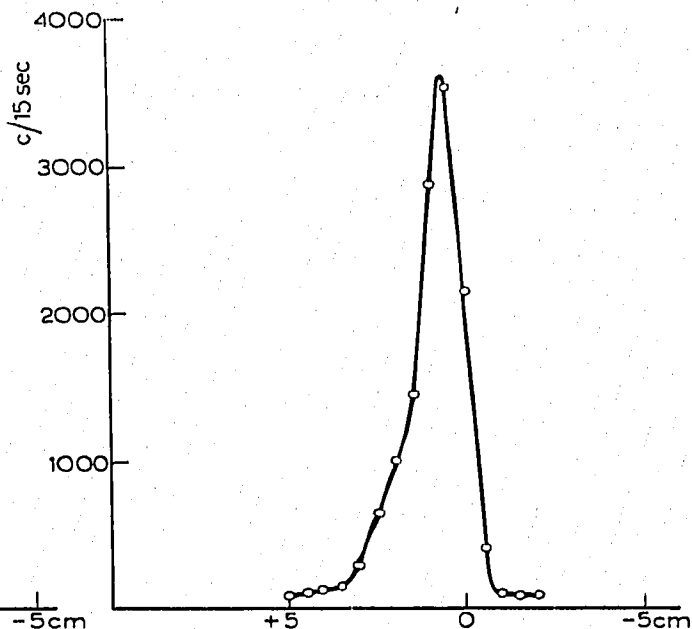


Fig. 10

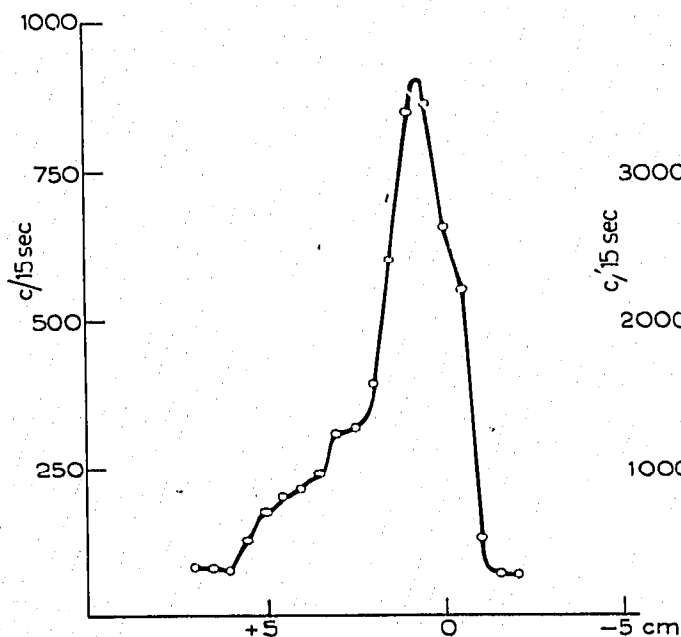


Fig. 11

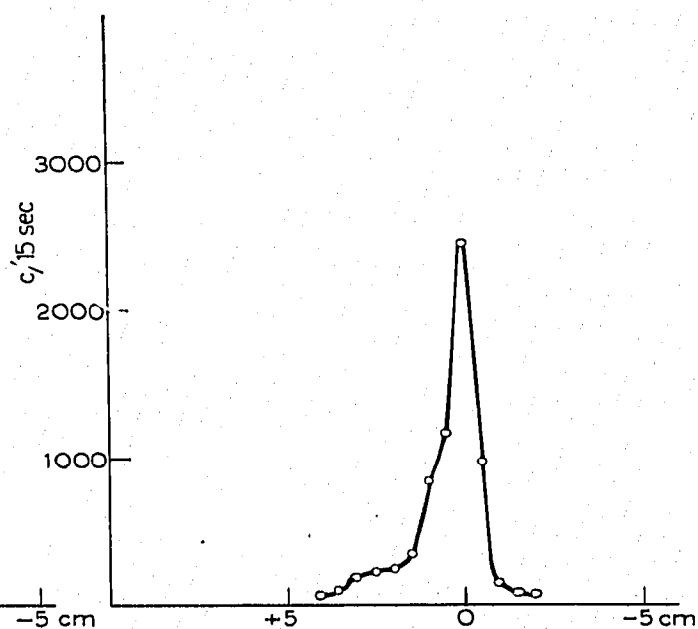


Fig. 12

Figs. 7-12. Paper electropherograms of protactinate. Conditions: (7) 1 hour, 250 V, electrolyte 1 N KOH, washed Whatman No. 1 paper, glass plates. (8) as (7) with Whatman glass fibre paper instead of No. 1 cellulose paper. (9) as (7), electrolyte: 1 N KOH containing 1% EDTA. (10) as (9) with plexiglass plates replacing the glass plates. (11) as (10), electrolyte: 0.1 N KOH containing 1% EDTA. (12) as (7), electrolyte: 0.1 N KOH, 1% EDTA and 1% K_3PO_4 .

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of protactinate followed by a drop of the metal ion solution on washed paper and developing with N KOH. When the activity is retained on the point of application or retarded this must be due to insolubilisation by the metal ion.

Some, but relatively little, precipitation occurred with Mg, Ti(IV) and Zr(IV). Almost complete retention at the start was obtained with La, Fe(III), Sr(II) and Tl(I). Complete precipitation occurred with Ba, Ca and Mn (which forms MnO_2).

VII. Stability of protactinate solutions to heating

Solutions of protactinate in $6 N$ KOH were placed on the water bath for one hour and developed with N KOH on washed Whatman No. 1 paper. The activity was always found on the liquid front, sometimes divided into two adjacent peaks (as is also often found in non-heated solutions), but no indication of precipitation due to heating could be noted.

VIII. Paper electrophoresis

As already shown in our preliminary note, protactinate moves somewhat to the anode on unwashed paper Whatman No. 1 with N KOH as electrolyte. On washed paper the movement is of the same order, *i.e.* the peak moves at the most 5 mm to the anode.

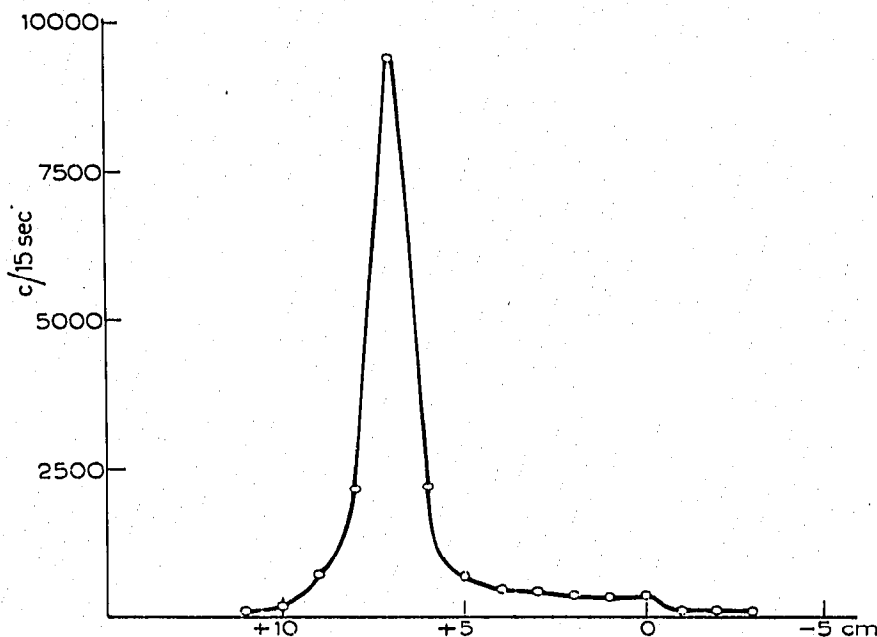


Fig. 13. Paper electropherogram of tracer $^{32}PO_4^{-3}$. Conditions: 1 hour, 250 V, electrolyte $0.1 N$ KOH containing 1% EDTA, washed Whatman No. 1 paper.

Prolonged electrophoresis indicated that the movement does not increase with time. Additions of EDTA did not increase the movement either, nor did electrophoresis on glass paper or on filter paper with perspex plates replacing the usual glass plates. Figs. 7-13 show the activity curves obtained. They also show the movement of $^{32}PO_4^{-3}$ tracer and the movement of protactinate in presence of 1% K_3PO_4 to inhibit adsorption (if any).

CONCLUSION

We may summarise the properties of protactinate solutions at tracer levels in alkali as follows: It is readily soluble in aqueous alkali, does not hydrolyse in 0.1 N KOH and is not decomposed when heated in solution to 100°. It is not extracted to any extent into butanol or methyl propyl ketone, nor adsorbed strongly on glass. It is precipitated by Ba, Sr, Ca, Tl(I) and coprecipitated with MnO₂, La and Fe(III). On Dowex-2 adsorption occurs and the adsorption equilibrium indicates that protactinate has a charge of three. However, the slow movement in paper electrophoresis is incompatible with the high charge exhibited in ion exchange. Orthophosphate tracer under the same conditions moves with a much higher speed. It is thus not possible from these tracer experiments to suggest a probable structure for the protactinate ion. The slow electrophoretic movement may be caused by the existence of the protactinate in a polymeric form or to ion pair formation with K⁺ ions, the latter being less likely than the former.

SUMMARY

The paper chromatography, paper electrophoresis, anion exchange, solvent extraction and precipitation reactions of tracer quantities of protactinate are described.

REFERENCE

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