The Hydrolysis of Acetic Anhydride. Part V. Catalysis by Strong Acids.*

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The influence of perchloric, sulphuric, and phosphoric acid on the hydrolysis velocity has been measured over a wide range of acidity. The acids, as well as hydrochloric acid (Part IV *), have a strong catalytic effect at high concentrations. The rate increases much more rapidly than the stoicheiometric concentration of acid or of hydrogen ion. In each case, the logarithm of the rate decreases approximately linearly with Hammett's acidity function H_0, the slopes lying in the range $-0{\cdot}7$ to $-1{\cdot}3$, but there are differences in behaviour between the different acids and deviations from linearity become apparent, particularly in the cases of perchloric and sulphuric acids, for which the solutions studied cover an acidity range of 4·1 units of H_0.

The observations are held to indicate that the transition state of the reaction does not contain a water molecule and to be consistent with a mechanism in which the rate-determining step is the formation of an acetylium ion from a protonated acetic anhydride molecule.

IT was suggested by Hammett (" Physical Organic Chemistry," McGraw Hill Book Co., p. 273; cf. Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791) that a proportionality between the reaction velocity of an acid-catalysed hydrolysis reaction and acidity function (h_0) is expected when the activated complex does not contain a water molecule, whereas the rate is expected to follow the stoicheiometric concentration of hydrogen ion if a water molecule is involved in the rate-determining step. The systematic application of this principle to the study of reaction mechanism, mainly by Long, has demonstrated the value of this method for a variety of reactions (hydrolysis of lactones: Long and Purchase, *J. Amer. Chem. Soc.*, 1950, **72**, 3267; Long, Dunkle, and McDevit, *J. Phys. Chem.*, 1951, **55**, 829; hydrolysis of methylal: Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3240, 3243; depolymerisation of trioxan: Paul, *ibid.*, 1952, **74**, 141; hydration of *iso*butene: Taft, *ibid.* p. 5372; depolymerisation of paraldehyde: Bell and Brown, *J.*, 1954, 774).

In the present investigation the dependence of the hydrolysis of anhydride upon acidity has been examined for several strong acids with the object of obtaining information concerning the mechanism of the catalysed reaction.

EXPERIMENTAL

Acetic anhydride was purified as in Part IV. Aqueous acids were made up from the purest samples of the acids obtained commercially. They were standardised either volumetrically or by density determinations.

Reaction velocities were determined either dilatometrically (Gold, Hilton, and Jefferson, *J.*, 1954, 2756) or by the thermal maximum method, as described in Part IV. Each dilatometric rate constant given is the mean of several determinations, agreeing within 4%. All measurements by the thermal method were repeated several times, as in Part IV. The reactions whose progress was followed dilatometrically were found to be accurately of first order, and rate constants were, as a rule, evaluated by Guggenheim's method (Fig. 1). Since the dilatometer level is sensitive to temperature changes, particular attention was paid to the elimination of the temperature difference which exists between the inside of a reaction vessel and the surrounding bath owing to the evolution of the heat of the reaction (cf. Luten, *J. Phys. Chem.*, 1935, **39**, 199; Tong and Olson, *J. Amer. Chem. Soc.*, 1943, **65**, 1704) or the attainment of the thermostat temperature after mixing. Even for a reaction with half-life as short as 2 min., the error from these sources was negligible, and significant readings could be obtained within a fraction of a minute of filling the dilatometer. It was assumed that the first-order

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* Part IV, preceding paper.

kinetics continue into the region where measurements were carried out by the thermal maximum method. The rate constants obtained by this method are values of k'_1, calculated from equation (2) of Part IV. For sulphuric acid the heat of mixing (T_i) with acetic anhydride was not detectable by our methods and, accordingly, the value of k'_1 should be close to the value of the rate constant k. This conclusion is supported by the continuity of the portions of the log k–H_0 curves determined by the two methods (Fig. 2). This continuity is also fairly direct evidence that the hydrolysis reaction is the rate process observed by the thermal maximum method. In the case of perchloric acid there is an apparent break in the curves of rate constants obtained by the two methods, but the following considerations show that this is almost certainly due to the neglect of T_i in the calculation of k'. It will be recalled (Part IV, Table 1, Fig. 2) that for positive values of T_i/T_0, the value of k' exceeds the value of the rate constant k, and that the deviation becomes more marked the lower the ratio (R) of the rate constant of the reaction to the Newton's law cooling constant of the vessel. For the experimental points corresponding to large values of R' (which, in this case, is a good approximation to R) it is found that there is a linear relation between log k' and H_0. The experimental points corresponding to smaller values of R' diverge from these lines in an upward direction in a similar manner to the way in which log R' diverges from log R (see Part IV, Fig. 2) if $\rho \sim 0{\cdot}15$. For this reason it is thought that no chemical significance attaches to the divergence of the lowest points (obtained by the thermal method) from the linear log k–H_0 graphs. These points have been marked † in Tables 1—3, and indicated by shading in Figs. 2 and 3. These reservations do not apply to the results at higher acidities.

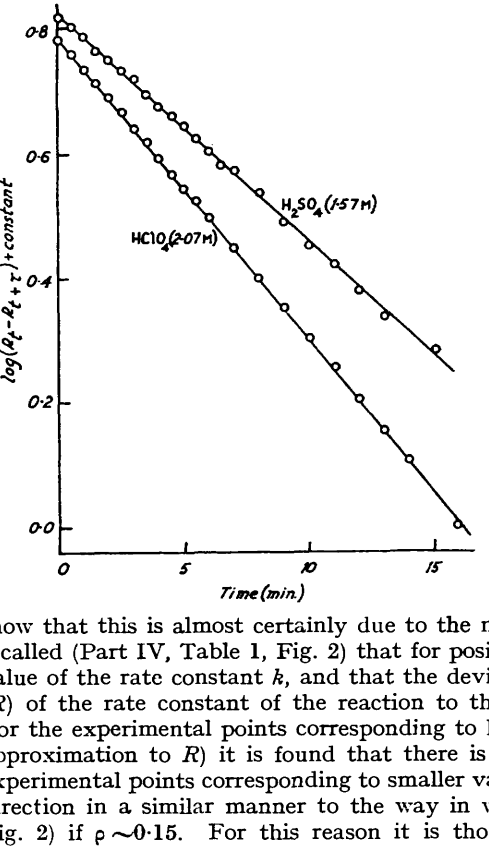

FIG. 1. *Illustration of first-order course of the hydrolysis of acetic anhydride in aqueous acids at* 0°.

Results

TABLE 1. *The hydrolysis of acetic anhydride in aqueous perchloric acid at* 0°.

A. By dilatometry.

$[Ac_2O]_{initial} = 0{\cdot}07$M (approx.).

$[HClO_4]$ (M *)	H_0	10^4k (sec.$^{-1}$)	$10^4k_{cat.}$‡ (sec.$^{-1}$)	log $k_{cat.}$ +5·0	$[HClO_4]$ (M *)	H_0	10^4k (sec.$^{-1}$)	$10^4k_{cat.}$ (sec.$^{-1}$)	log $k_{cat.}$ +5·0
0·00	—	4·60	—	—	1·29	−0·01	9·78	5·18	1·71
0·203	0·85	5·26	0·66	0·82	1·49	−0·13	11·2	6·6	1·82
0·400	0·75	5·76	1·16	1·06	1·70	−0·25	13·7	9·1	1·96
0·585	0·51	6·41	1·81	1·26	1·90	−0·35	15·7	11·1	2·05
0·775	0·36	6·95	2·35	1·37	2·07	−0·42	18·3	13·7	2·14
0·95	0·22	8·10	3·50	1·54	2·29	−0·52	22·7	18·1	2·26
1·15	0·08	9·02	4·42	1·65	2·57	−0·64	29·9	25·3	2·40

* In this and subsequent Tables, concentrations so denoted are stoicheiometric.

‡ $k_{cat.} = k_1 - k_1{}^{\circ}$ and $k'_{cat.} = k' - k_1{}^{\circ}$, where $k_1{}^{\circ}$ = first-order rate constant in water.

TABLE 1. (*Continued.*)

B. By thermal maximum method.

$[Ac_2O]_{initial} = 0{\cdot}01$—$0{\cdot}04$M.

$[HClO_4]$ (M)	H_0	10^2k_2 (sec.$^{-1}$)	t_m (sec.)	$10^2k'$ (sec.$^{-1}$)	$10^2k'_{cat.}$	$\log k'_{cat.} + 5{\cdot}0$
2·68	−0·68	1·36	92	0·85	0·80	2·90 †
3·12	−0·88	1·68	76	1·01	0·96	2·98 †
		1·92	70	1·02	0·97	2·99 †
3·54	−1·08	2·02	58	1·47	1·42	3·15 †
3·57	−1·09	2·00	60	1·44	1·39	3·14 †
		1·54	69	1·37	1·32	3·12 †
4·01	−1·30	1·79	48	2·45	2·40	3·38
		1·31	56	2·45	2·40	3·38
4·43	−1·51	2·04	34	4·2	4·2	3·62
5·32	−1·94	1·55	17·7	14·0	14·0	4·15
5·80	−2·20	2·10	9·2	33	33	4·52

† Points in shaded area of Figs. 2 and 3.

TABLE 2. *The hydrolysis of acetic anhydride in aqueous sulphuric acid at* 0°.

A. By dilatometry.

$[Ac_2O]_{initial} = 0{\cdot}07$M (approx.)

$[H_2SO_4]$ (M)	H_0	h_0	10^4k (sec.$^{-1}$)	$10^4k_{cat.}$ (sec.$^{-1}$)	$\log k_{cat.} + 5{\cdot}0$
0·00	—	—	4·60	—	—
0·127	0·89	0·13	5·99	1·39	1·14
0·223	0·45	0·35	6·60	2·00	1·30
0·443	0·28	0·52	7·87	3·27	1·51
0·54	0·19	0·65	8·37	3·77	1·58
0·74	0·06	0·87	9·33	4·73	1·67
0·99	−0·12	1·32	10·6	6·0	1·78
1·17	−0·23	1·70	11·6	7·0	1·85
1·36	−0·35	2·24	12·5	7·9	1·90
1·56	−0·47	2·95	13·8	9·2	1·96
2·05	−0·74	5·50	19·0	14·4	2·16
2·30	−0·88	7·59	24·6	20·0	2·30
2·44	−0·95	8·91	26·2	21·6	2·33

B. By thermal maximum method.

$[Ac_2O]_{initial} = 0{\cdot}01$—$0{\cdot}04$M.

$[H_2SO_4]$ (M)	H_0	10^3k_2 (sec.$^{-1}$)	t_m (sec.)	$10^2k'$ (sec.$^{-1}$)	$10^2k'_{cat.}$ (sec.$^{-1}$)	$\log k'_{cat.} + 5{\cdot}0$
2·96	−1·20	1·43	124	0·40	0·35	2·54 †
3·70	−1·53	1·88	83	0·72	0·68	2·83
4·44	−1·87	1·79	61	1·51	1·46	3·16
5·18	−2·21	1·83	38	3·6	3·6	3·56
5·92	−2·57	1·69	25	7·8	7·8	3·89
6·65	−2·98	1·84	14·5	17·3	17·3	4·24
7·40	−3·36	1·86	8·8	35·0	35·0	4·54

TABLE 3. *The hydrolysis of acetic anhydride in aqueous phosphoric acid at* 0°.

By thermal maximum method.

$[Ac_2O]_{initial} = 0{\cdot}01$—$0{\cdot}04$M.

$[H_3PO_4]$ (M)	H_0	10^2k_2	t_m (sec.)	$10^2k'$ (sec.$^{-1}$)	$10^2k'_{cat.}$ (sec.$^{-1}$)	$\log k'_{cat.} + 5{\cdot}0$
7·62	−1·28	1·70	70	0·82	0·77	2·89 †
8·27	−1·47	1·60	60	1·30	1·25	3·08 †
8·90	−1·69	2·05	52	1·90	1·85	3·24 †
9·54	−1·95	1·51	46	3·0	3·0	3·48
10·20	−2·15	1·64	34	4·7	4·7	3·67
10·80	−2·36	1·78	27	6·6	6·6	3·82
11·45	−2·62	1·84	19	11·5	11·5	4·06
12·72	−3·10	1·72	10	30	30	4·48

DISCUSSION

1. *The Dependence of Reaction Velocity upon Acidity.*—The relation between the logarithm of the catalytic coefficient and the acidity function H_0 is shown in Fig. 2, which includes all experimental values for acetic anhydride of the present paper and Part IV. A broken line of *unit slope* has been drawn through the points. In Fig. 3 the experimental points for the monobasic acid $HClO_4$ have similarly been plotted against log $[HClO_4]_{stoich.}$ * and, again, a straight line of unit slope has been included in the Figure (see also Part IV, Fig. 3). Although neither of the two broken lines is a perfect representation of the

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* For perchloric acid, $[HClO_4]_{stoich.} \approx [H_3O^+]$ (Redlich, *Chem. Rev.*, **1946, 39, 333**).

experimental points there can be no doubt as to which of the two is a better approximation. The catalytic coefficient is clearly not proportional to the stoicheiometric concentration of perchloric acid or hydrogen ion. The slope of the experimental points in Fig. 3 is nowhere constant and at the highest acidities exceeds the theoretical slope by a *factor* of about 9. On the other hand, log k follows the acidity function H_0 very closely at low acidities and over no significant range is the numerical value of the slope of the graph more than 30% removed from unity. The differences in behaviour of the various acids and the departures from linearity which are present, particularly at high acidities, are more in the nature of deviations from a limiting law and will be further discussed below.

These departures may seem to be more marked in the present study than in previously studied cases where a rate of dependence upon H_0 has been established, but it should also be remembered that the range of the experimental points contained in Fig. 2 (representing an approximately 10^4-fold variation in the catalysed rate) is much more extensive than is usual for this type of investigation. If the shorter (forty-fold) range of catalytic rate constants covered by the dilatometric measurements alone is considered, the deviations are much less pronounced and, if we restrict our attention to the dilatometric results for perchloric acid, the agreement with the theoretical curve is almost perfect.

FIG. 2.

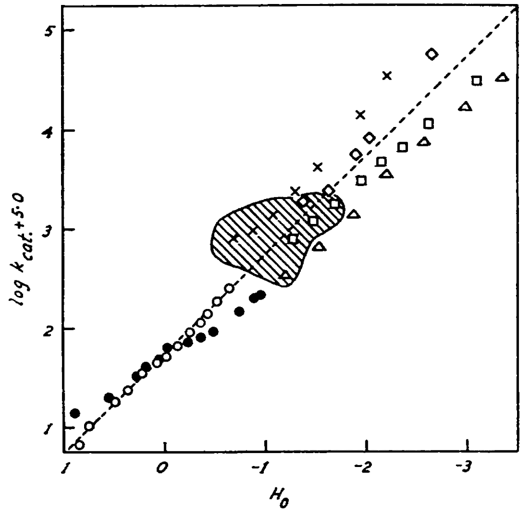

FIG. 3.

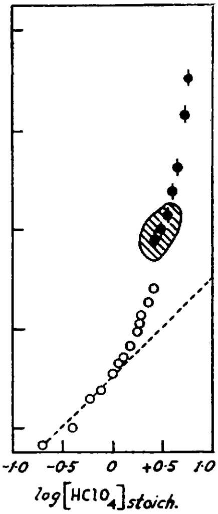

FIG. 2. *Dependence of reaction velocity on acidity function H_0.*

○ $k_{cat.}$, $HClO_4$ (dilatometry).
× $k'_{cat.}$, $HClO_4$ (thermal maximum method).
● $k_{cat.}$, H_2SO_4 (dilatometry).
△ $k'_{cat.}$, H_2SO_4 (thermal maximum method).
□ $k'_{cat.}$, H_3PO_4 („ „ „).
◇ $k'_{cat.}$, HCl („ „ „).

FIG. 3. *Dependence of reaction velocity on concentration of perchloric acid.*

○ Dilatometry. ⧫ Thermal maximum method.

2. *The Mechanism of the Catalysis.*—The observation that log k follows H_0 more closely than log $[H_3O^+]$ implies, on the basis of the principle mentioned, that a water molecule is not involved in the transition state. A water molecule would, of course, be involved for the transition state of the $A_{Ac}2$ mechanism

$$Ac_2O + H^+ \rightleftharpoons Ac_2OH^+ \text{ (rapid)}$$

$$H_2O + Ac_2OH^+ \longrightarrow (X^+) \longrightarrow CH_3{\cdot}CO_2H + CH_3{\cdot}CO_2H_2^+ \text{ etc. (rate-controlling)}$$

where (X^+) is the activated complex of the rate-controlling step. {It would be possible to reconcile approximate parallelism between log k and $-H_0$ with this mechanism if, contrary to Hammett's suggestion, it were assumed that $f_{Ac.OH^+}/f_{X^+}$ = constant. On that assumption, log $k_{\mathrm{cat.}}$ for the $A_{\mathrm{Ac}}2$ mechanism should parallel $-[H_0 - \log (\mathrm{H_2O})]$, which, over the concentration range studied, is not very different from $-H_0$. By analogy with the case of lactone hydrolysis this assumption concerning activity coefficients and interpretation of the mechanism seems much less likely than the conclusion that a water molecule does not participate in the rate-controlling step.}

The simplest and most probable mechanism compatible with Hammett's principle is an $A_{\mathrm{Ac}}1$ mechanism:

$$\mathrm{Ac_2O + H^+ \rightleftharpoons Ac_2OH^+} \quad \text{(rapid)}$$

$$\mathrm{Ac_2OH^+ \longrightarrow (Y^+) \longrightarrow Ac^+ + AcOH} \quad \text{(rate-controlling)}$$

$$\mathrm{Ac^+ + 2H_2O \longrightarrow AcOH + H_3O^+} \quad \text{(rapid)}$$

where Y^+ is the activated complex of the rate-controlling step.

3. *The Deviations from an Exact Dependence of log* k *upon* $-\mathrm{H}_0$.—No exact interpretation can be given of the observation that there are marked differences between the behaviour of the various strong acids studied. These are only to a minor extent due to the neglect of the heat of mixing in deriving the rate constants k' for the thermal maximum method and the observations probably have a chemical basis. The following considerations seem relevant:

(a) *Temperature effect upon* H_0. For experimental reasons the velocity measurements were carried out at 0°, whereas the acidity function H_0 has been determined only for a temperature of 25°. A fuller explanation may be possible when the acidity functions at 0° are known. The temperature changes would probably affect the acidities of the various acids differently. It may be significant in this connection that the deviations of the experimental points for the viscous and associated acids, sulphuric acid and phosphoric acid, are in the direction of decreased acidity at the lower temperature, whereas the monobasic unassociated acids, hydrochloric and perchloric acids, diverge in the opposite direction.

(b) *Constancy of activity coefficient terms.* Long and McIntyre (*loc. cit.*) have focused attention on the fact the the parallelism between the acidity function and log k will only be exact in the absence of salt effects, *i.e.*, if the ratio $f_{\mathrm{Ac_2O}}f_{\mathrm{BH^+}}/f_{\mathrm{Y^+}}f_{\mathrm{B}}$ is exactly constant, where B,BH$^+$ is the conjugate acid–base pair used in the determination of the acidity function. They have shown that explicit recognition of the influence of a salt effect by the catalyst acid itself on this ratio allows an improvement in the agreement for the hydrolysis of methylal. In first approximation the modified relation between log k and H_0 may be stated in the form

$$\log k = -H_0 + (\alpha_{\mathrm{Ac_2O}} - \alpha_{\mathrm{B}})\,[\mathrm{Acid}] + \mathrm{const.}$$

where $\alpha_{\mathrm{Ac_2O}}$ and α_{B} are the salting-out parameters defined by the equation

$$\log f_{\mathrm{B}} = \alpha_{\mathrm{B}} \times [\mathrm{Acid}]$$

Owing to the large spontaneous rate of hydrolysis of acetic anhydride the determination of the salting-out parameter would be very difficult and has not been carried out. Consequently, we are uncertain how great an improvement the specific inclusion of this effect would bring about. In the main it would tend to change the slope of the log k–H_0 graphs more than their curvature.

(c) *The behaviour of sulphuric acid.* It follows algebraically that if log $k + H_0$ is constant, k must be directly proportional to h_0. This direct plot is more sensitive to experimental deviations from the exact relation than the logarithmic graph, particularly at high concentration. In accordance with this expectation, the graph of k against h_0 for perchloric acid is found to be linear at the low-concentration end of the scale, the intercept passing through the ordinate at the value of k corresponding to the spontaneous rate. Fig. 2 shows that the points for sulphuric acid and for perchloric acid fall on the same line up to an acidity of $H_0 = ca.\ -0{\cdot}1$. After this, the points for sulphuric acid are lower than those for perchloric acid, but for $H_0 < ca.\ -0{\cdot}6$ a straight line of slope 0·93 can be drawn through the points. The experimental points may equally well be held to fall on two straight lines meeting at $H_0 = -1$ and having slopes of 0·64 and 0·96, respectively, or to follow an S-shaped curve. This behaviour is shown much more clearly in the graph of k against h_0 for sulphuric acid, going up to an acidity $H_0 = -1$ only (Fig. 4). {In spite of these deviations the correlation of log k with log $[H_2SO_4]$ or log $[H_3O^+]$ by using Young's data (" Record of Chemical Progress," Spring Issue, 1951, 81) is much less satisfactory.} The chemical interpretation of these observations is not certain. They are believed to be connected with a specific effect of sulphate or bisulphate ions.

4. *The State of Acetic Anhydride in Concentrated Sulphuric Acid.*—The mechanism proposed for the acid-catalysed hydrolysis of acetic anhydride involves the rate-determining unimolecular heterolysis of the species Ac_2OH^+. The acetylium ions (Ac^+) formed by this reaction are then hydrated rapidly, *i.e.*, they do not persist in solution in appreciable concentration. As the acid concentration increases, the activity of water in the solvent decreases, and the extent to which the acetylium ions are hydrated will be governed by the equilibrium constant for the hydration reaction $Ac^+ + H_2O \rightleftharpoons AcOH_2^+$. It is not possible to decide, on the basis of the present experiments, whether this equilibrium lies to the right or to the left in 100% sulphuric acid (where the activity of water is small but finite owing to the self-dehydration equilibrium $2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$) (Brand, *J.*, 1946, 585; Gillespie, *J.*, 1950, 2516). However, it is known that acetic acid produces a two-fold freezing-point depression in sulphuric acid (Hantzsch, *Z. physikal. Chem.*, 1907, **61**, 257), *i.e.*, the ion $AcOH_2^+$ is not dehydrated. This result could have the kinetic reason that the rate of the dehydration reaction is extremely small, and it is only on this basis that Gillespie's explanation of the four-fold freezing-point depression of acetic and benzoic anhydride in 100% sulphuric acid (*J.*, 1950, 2997) is intelligible. In Gillespie's paper it is assumed that $CH_3{\cdot}CO^+$ ions are not hydrated and $CH_3{\cdot}CO_2H_2^+$ ions are not dehydrated in 100% sulphuric acid. This kinetic argument does not seem attractive when it is remembered that no time effect was detected in the freezing-point of solutions of 3 : 5-dibromo-2 : 4 : 6-trimethylbenzoic acid in sulphuric acid, where acylium and acidium ions coexist (Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 708). Further, the limited number of measurements on oxygen-isotope exchange in carboxylic acids show that it is strongly acid-catalysed (Roberts, *J. Chem. Phys.*, 1938, **6**, 294; Senkus and Brown, *J. Org. Chem.*, 1938, **2**, 569) and it does not therefore seem likely that the rupture of a C–O bond is immeasurably slow in 100% sulphuric acid. These arguments suggest that the question of the state of acetic anhydride in sulphuric acid has not been settled (cf. Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40).

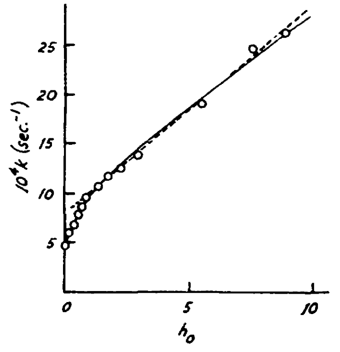

FIG. 4. *Catalytic effect of sulphuric acid at low concentrations.*

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