110. *The Hydrolysis of Triphenylmethyl Chloride in Dioxan.*

By DENNIS R. READ and WILLIAM TAYLOR.

Triphenylmethyl chloride is known to ionise in solvents such as liquid sulphur dioxide. Its hydrolysis might therefore be expected to proceed through a unimolecular mechanism involving slow ionisation (Hughes and Ingold) and should on this basis be of the first order with respect to the chloride but not to water. However, it is now found that the reaction is of the first order with respect to *both* triphenylmethyl chloride and water. Hence, neither the above unimolecular ionisation mechanism

nor Hammett's multimolecular mechanism can be operative. It is concluded that the reaction proceeds through Taylor's bimolecular mechanism (S_m).

Further, in many previous investigations on the hydrolysis of alkyl halides not involving the use of soluble bases, water has been found to have a high accelerating effect. We report that triphenylmethyl chloride exerts a still higher catalytic effect than water on its own hydrolysis. The solvent theories of (*a*) Hughes and Ingold, (*b*) Hammett, and (*c*) Taylor, which were based on the former effect only, are shown to be inadequate for the interpretation of the latter effect.

Nixon and Branch (*J. Amer. Chem. Soc.*, 1936, **58**, 492) measured conductometrically the rate of alcoholysis of triphenylmethyl chloride at 0° and 25° in ether–alcohol (60 : 40 by vol. at 25°). Over the very low concentration range of triphenylmethyl chloride used, *viz.*, 0·002—0·0001 g.-mol./l., they found that the reaction was of the first order with respect to the chloride. They pointed out that the high concentration of alcohol in their experiments prevented any attempt being made to distinguish between a unimolecular ionisation mechanism of the type of Gleave, Hughes, and Ingold (J., 1935, 236), in which alcohol merely plays the part of an ionising solvent, and a bimolecular mechanism in which alcohol is a direct reagent.

Since Walden (*Ber.*, 1902, **35**, 2023) has shown that triphenylmethyl chloride ionises in liquid sulphur dioxide, possibly owing to solvation of the cation,

$$\mathrm{CPh_3Cl} \xrightarrow{\mathrm{SO_2}} \overset{\oplus}{\mathrm{C}}\mathrm{Ph_3{\cdot}SO_2} + \overset{\ominus}{\mathrm{Cl}}$$

(Walden, 3rd Solvay Report, 1928, p. 510; Ingold, *Trans. Faraday Soc.*, 1938, **34**, 225; Sidgwick, see Waters, " Physical Aspects of Organic Chemistry," 1937, p. 189), this suggests strongly that the alcoholysis or hydrolysis of this compound might proceed through the unimolecular ionisation mechanism, *i.e.*,

$$\mathrm{CPh_3Cl} \xrightarrow[\text{(slow)}]{\mathrm{H_2O}} \underset{\text{(solvated)}}{\overset{\oplus}{\mathrm{C}}\mathrm{Ph_3}} + \overset{\ominus}{\mathrm{Cl}}$$

$$\underset{\text{(solvated)}}{\overset{\oplus}{\mathrm{C}}\mathrm{Ph_3}} + \mathrm{H_2O} \xrightarrow[\text{(rapid)}]{} \mathrm{CPh_3{\cdot}OH} + \underset{\text{(solvated)}}{\overset{\oplus}{\mathrm{H}}}$$

If this were so, the reaction would be of the first order with respect to triphenylmethyl chloride alone, and would show no clear-cut dependence on the concentration of water. However, increasing concentrations of water would be expected to increase the rate of hydrolysis in a general way owing to increased facility of ionisation.

On the other hand, Olson and Halford (*J. Amer. Chem. Soc.*, 1937, **59**, 2644) and Taylor (J., 1937, 344, 992, 1853, 1962; J., 1938, 840; *J. Amer. Chem. Soc.*, 1938, **60**, 2094) advance evidence suggesting that the hydrolysis of alkyl halides invariably follows a bimolecular mechanism, *i.e.*, $\mathrm{CPh_3{\cdot}Cl} + \mathrm{H_2O} \longrightarrow \mathrm{CPh_3{\cdot}OH} + \mathrm{HCl}$, in which circumstance the reaction should be of the first order with respect to both reagents. A third proposed mechanism is that of Hammett and his co-workers (*J. Amer. Chem. Soc.*, 1937, **59**, 2536, 2542), who regard the hydrolysis of alkyl halides as being multimolecular, involving the participation of several water molecules for each molecule of halide :

$$\mathrm{CPh_3{\cdot}Cl} + n\mathrm{H_2O} \longrightarrow \mathrm{CPh_3{\cdot}OH} + \overset{\oplus}{\mathrm{H}}\mathrm{_3O} + \overset{\ominus}{\mathrm{Cl}}\ \text{(solvated)}$$

This view is taken, partly at least, because high concentrations of water are required to effect hydrolysis and because at these concentrations of water the rate of hydrolysis appears to be proportional to several powers of the concentration of water.

It is clear, therefore, that the elucidation of the mechanism of hydrolysis (and of solvolysis generally) of alkyl halides by means of kinetics investigations has been rendered difficult because, in general, a relatively high concentration of water is required to effect reaction at a measurable rate, and this prevents any real significance being attached to the results of the application of the law of mass action (see, *e.g.*, Lewis, " A System of Physical Chemistry," 1929, p. 186). Tertiary halides are, however, reactive enough to allow sufficiently small concentrations of water to be used (Taylor, J., 1937, 1853; *J. Amer.*

Chem. Soc., 1938, **60**, 2094), but the difficulty of finding a solvent inert to both reactants and products then arises; *e.g.*, acetone is unsuitable owing to complications (*loc. cit.*). However, dioxan has now been found to be very suitable.

The purpose of this investigation was to determine whether or not the reaction between triphenylmethyl chloride and water in dioxan solution, the two reagents being present in low concentrations, was of the first order with respect to each of them. The reaction at 50° was followed by a titrimetric method. From Table I it is seen that for concentrations of 0·1—0·2 g.-mol./l.for the halide and 0·1—0·5 g.-mol./l. for water, *i.e.*, within the space enclosed by the broken line, the second-order velocity coefficient is constant within the limits of experimental error. Thus

$$\text{reaction rate} = \text{const.}\ [CPh_3{\cdot}Cl][H_2O]$$

or, for a range of concentrations of both reagents for which the law of mass action is commonly assumed to apply, the hydrolysis *is* of the first order with respect to each reagent.

TABLE I.

Mean Values of the Second-order Velocity Coefficients (100k, *expressed in l. g.-mol.*$^{-1}$ *min.*$^{-1}$) *at* 50°.

	$[H_2O]$.							
$[CPh_3Cl]$.	0·1213.	0·1713.	0·2213.	0·3713.	0·5213.	0·6213.	1·0213.	2·0213.
0·1000	2·03	1·90	2·13	2·12	2·12	2·52	5·24	21·6
0·1500	2·05	2·05	2·11	2·18	2·49			
0·2000	2·02	—	2·10	2·36	3·49			
0·5000	4·97							
0·6000	6·33							

This affords unambiguous evidence that, within these limits and under these conditions, the hydrolysis of triphenylmethyl chloride proceeds through a mechanism which is neither a unimolecular ionisation (Hughes and Ingold) nor multimolecular (Hammett) but bimolecular. This is presumably of the London type (*Z. Elektrochem.*, 1929, **35**, 552), involving simultaneous addition and dissociation of the reagents as pictured in more detail in the mechanism (S_m) discussed by Taylor (J., 1937, 1965).

Solvent Effect.—The value of the second-order velocity coefficient increases rapidly as $[H_2O]$ exceeds 0·5 g.-mol./l. (Table I). Any one of the three hypotheses which have been put forward might interpret such an effect, which is general for the hydrolysis of alkyl halides where no strong soluble base is present. These are (i) that of Hughes and Ingold (J., 1935, 244), who attribute it to an increased facility of ionisation of the alkyl halide due to increased water concentration; (ii) that of Hammett (*loc. cit.*), who regards the hydrolysis as being multimolecular with respect to water, one molecule of the halide reacting with several molecules of water owing to the affinity of the water molecules for halide ion; and (iii) that of Taylor (J., 1938, 840), who regarded it as being due to the added water causing increased dissociation of the water already present into a simpler and more reactive form.

None of these can be the correct intepretation, at least for triphenylmethyl chloride, since it is now found (Table I) that the value of the second-order velocity coefficient increases with increasing concentrations of triphenylmethyl chloride above 0·2 g.-mol./l., and the effect is even greater than that due to water. On theory (i) this would presumably be attributed to an increase in the ionising power of the solvent, part of which is the halide, leading to increased facility of ionisation of the solute which now must be regarded as being water. In other words the hypothesis that an inert solvent, water, facilitates ionisation of the halide must, on this new observation, lead to the diametrically opposite view that water is not inert but is acted on by the halide in the rate-determining stage of the reaction. Theory (ii) would lead to the view that several molecules of the halide react with one molecule of water, in which case it would be difficult to ascribe the effect to the driving force of the solvation of hydrogen ions or hydroxyl ions by triphenylmethyl chloride molecules. From theory (iii) it would be inferred that alkyl halides are associated in solution, which is palpably incorrect.

The true interpretation must lie in the increased total concentration of the reagents being above the maximum necessary for the application of the law of mass action. The excess reagents may then assume the rôle of solvent.

The Reversibility of the Reaction.—The reaction is reversible and may be represented stoicheiometrically by :

$$\mathrm{CPh_3Cl + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CPh_3{\cdot}OH + HCl}$$

since triphenylcarbinol was isolated in almost quantitative yield from the products of the forward reaction, and triphenylmethyl chloride in high yield from the reverse reaction. Unfortunately, the rate of the reverse reaction, under conditions corresponding to those of the forward reaction, was so high as to preclude any possibility of its measurement by our titrimetric method. However, the equilibrium constants derived from the experimentally observed equilibrium concentrations of hydrogen chloride for the forward and the reverse reaction were approximately equal (Table II). This confirms the view that the only reactions occurring are as represented. Incidentally, an increase in the concentration of water increases the value of the equilibrium constant, which appears to be generally true for such systems (see, *e.g.*, J., 1937, 1853). In Table II, $[\mathrm{HCl}]_{\mathrm{eq.}}$ represents the experimentally observed equilibrium concentration of hydrogen chloride (corrected, as described on p. 482).

TABLE II.

Showing the Approximate Equality of $K = [\mathrm{CPh_3{\cdot}OH}][\mathrm{HCl}]/[\mathrm{CPh_3{\cdot}Cl}][\mathrm{H_2O}]$ *as Determined for the Forward and for the Reverse Reaction, and hence the True Reversibility of the Reaction.*

Reverse reaction.

Initial concns.					Initial concns.				
$[\mathrm{CPh_3{\cdot}OH}]$.	[HCl].	$[\mathrm{H_2O}]$.	$[\mathrm{HCl}]_{\mathrm{eq.}}$.	*K*.	$[\mathrm{CPh_3{\cdot}OH}]$.	[HCl].	$[\mathrm{H_2O}]$.	$[\mathrm{HCl}]_{\mathrm{eq.}}$.	*K*.
0·1000	0·1000	0·5213	0·0669	0·242	0·1500	0·2000	0·5213	0·1260	0·217
0·1000	0·1500	0·5213	0·1062	0·221	0·2000	0·1000	0·5213	0·0481	0·240
0·1000	0·2000	0·5213	0·1449	0·205	0·2000	0·1500	0·5213	0·0776	0·231
0·1500	0·1000	0·5213	0·0571	0·253	0·2000	0·2000	0·5213	0·1132	0·224
0·1500	0·1500	0·5213	0·0900	0·232	0·1000	0·1000	1·0213	0·0786	0·277
				Forward reaction.					
$[\mathrm{CPh_3Cl}]$.					$[\mathrm{CPh_3Cl}]$.				
0·1000	—	0·5213	0·0598	0·193	0·1000	—	1·0213	0·0733	0·212
0·1500	—	0·5213	0·0790	0·199	0·1000	—	2·0213	0·0830	0·287
0·200	—	0·5213	0·0940	0·195					

EXPERIMENTAL.

Triphenylmethyl chloride had m. p. 110—110·5° (Found : Cl, 12·6. Calc. : Cl, 12·7%). Triphenylmethylcarbinol had m. p. 157—157·5°. Dioxan was refluxed over metallic sodium for 3 days and distilled from this; b. p. 101·4—101·6°/760 mm.

Reaction Products.—(a) *Forward reaction.* Triphenylmethyl chloride (2·955 g.) was dissolved in dioxan (100 ml.) and water (2 g.), and the solution kept at 50° for 49 hours. Powdered chalk (5 g.) was added, the liquid filtered, and evaporated to constant weight at 50° in a vacuum. The residue (2·762 g.) had m. p. 154·5—155·5° and contained no trace of chloride. Recrystallisation of 1·511 g. from benzene gave a product (1·496 g.) of m. p. 157—157·5°, mixed m. p. with authentic triphenylmethylcarbinol 157—157·5°. This represents a quantitative conversion of chloride into carbinol.

(b) *Reverse reaction.* Triphenylmethylcarbinol (2·660 g.) was dissolved in dioxan (50 ml.), the solution saturated with dry hydrogen chloride, kept at 50° for 22 hours, and evaporated as in (a). The residue (2·830 g.) had m. p. 101·5—102° (Found : Cl, 11·1%). This represents 86% conversion of carbinol into chloride in the presence of the water generated during the reaction.

Kinetic Experiments.—*Procedure.* Flasks were calibrated to hold at 20° that volume of dioxan which at 50° became 50 ml., and pipettes were calibrated for 5 ml. under the same conditions. The flasks and pipettes were always dried by alcohol–ether before use. In making up the mixtures for the forward reaction, a weighed amount of water was added to dioxan containing a weighed amount of triphenylmethyl chloride in a calibrated flask, and the liquid made up to volume with dioxan. For the reverse reaction, a weighed amount of triphenylmethylcarbinol was dissolved in some dioxan in a calibrated flask; then a weighed amount of water, followed by an accurately measured volume of a standard dioxan solution of dry hydrogen chloride, were added, and the liquid made up to volume with dioxan. Aliquot portions were immediately pipetted into steamed test-tubes which had been dried at 120° for 4 hours and left overnight over calcium chloride in a desiccator. The tubes were then hermetically sealed and placed for protection in stout, fairly tightly-fitting tubes in a thermostat at 50°. The process from the time of mixing of the reagents to immersion in the bath occupied a fairly constant time of 10 minutes, the approximate temperature during this time being 20°. To follow the appearance or disappearance of acidity, at suitable times a tube was broken in a stoppered bottle containing an accurately measured mixture of benzene (100 ml.) and water (5 ml.), the liquid was well shaken, set aside until the aqueous layer was clear (2—5 mins.), and then this layer was run off. The bottle was washed out with benzene (20 ml.) and water (5 ml.); this was drained into the foregoing benzene layer, and the shaking, etc., repeated. The combined aqueous extract (10 ml.) was titrated against N/20-sodium hydroxide.

Extraction corrections. (*a*) The foregoing procedure failed to remove all the hydrogen chloride, for some was retained by the benzene; a correction factor of 1·12 was found, by control experiments, to be necessary.

(*b*) Further, a correction had to be applied for the slight degree of hydrolysis of triphenylmethyl chloride during the extraction process. The extent of the correction was found by determining the acidity liberated during this process from standard solutions of triphenylmethyl chloride in dioxan, with the following results (expressed in g.-mols./l.):

[CPh$_3$Cl]	0·0500	0·1000	0·1500	0·2000	0·3000	0·4000	0·5000	0·6000
Correction (*b*)	0·0008	0·0019	0·0022	0·0025	0·0032	0·0039	0·0050	0·0061

A smooth curve was constructed from these results, so that correction (*b*) could be ascertained for any value of [CPh$_3$Cl] within this range.

Finally, the correct concentration of hydrogen chloride present in the dioxan reaction liquid at time *t* was given by

$$[\mathrm{HCl}](\mathrm{corr.}) = 1{\cdot}12\{[\mathrm{HCl}](\mathrm{obs.}) - \text{correction } (b)\}$$

From this, the true reversibility of the system being assumed, the concentrations of all the other compounds present in the system could be found.

Correction for the Small Amount of Extraneous Moisture present in the Reaction Liquid.—Although rigid and systematic precautions were taken against the inclusion of extraneous moisture in the dioxan reaction systems, a very small constant amount was always present. This was demonstrated by using dry dioxan alone in the forward reaction. There was a gradual small increase in acidity until a constant value was reached, denoting equilibrium as shown below:

[CPh$_3$Cl] = 0·3000; [H$_2$O] (added) = 0·0000.

t (mins.)	5·5	11·5	17·5	26·5	37·5	∞
[HCl] (obs.)	0·0058	0·00715	0·00831	0·01030	0·01270	0·01550
Corrn. (*b*)	0·0032	0·0032	0·0032	0·0032	0·0032	0·0031
[HCl] (obs.) − (*b*)	0·0026	0·00395	0·00511	0·0071	0·0095	0·0124
[HCl] (corr.)	0·0029	0·0044	0·0057	0·0080	0·0106	0·0139

By employing different initial concentrations of triphenylmethyl chloride where [H$_2$O] (added) was 0·1000 and also 0·0000, the value of *c*, the concentration of the extraneous water was obtained as follows:

$$\begin{array}{ccccccc} \mathrm{CPh_3{\cdot}Cl} & + & \mathrm{H_2O} & \rightleftharpoons & \mathrm{CPh_3{\cdot}OH} & + & \mathrm{HCl} \\ (b-x) & & \{(0{\cdot}1+c)-x\} & & x & & x \end{array}$$

Hence $K = x^2/(b-x)(c-x) = x_1^2/(b-x_1)(0{\cdot}1+c-x_1)$

where x and x_1 are the equilibrium concentrations of hydrogen chloride and K is the equilibrium constant. The results are below:

b.	*x*.	x_1.	*c* (calc.).	*b*.	*x*.	x_1.	*c* (calc.).
0·6000	0·0192	0·0598	0·0255	0·2000	0·0128	0·0449	0·0177
0·3000	0·0139	0·0516	0·0179	0·1000	0·0119	0·0297	0·0240
							Mean 0·0213

This correction was applied in all experiments (see, *e.g.*, Table II).

The Determination of t_0.—The determination of t_0 became important when the reaction was as rapid as in the present series of experiments, t_0 being that point of time which could be taken as zero time for the reaction if the reaction liquid immediately after the reagents were mixed had attained a temperature of 50°. In our procedure, some reaction occurred both (*a*) during the 10 mins. for which the reaction liquid was at room temperature (20°) and also (*b*) whilst it was being heated to 50°. The problem to be solved was thus to determine what period of time at 50° would produce the same amount of reaction. (The time of immersion, being more definite than that of mixing, was a more convenient fiducial time.) For this purpose it was necessary to determine the temperature coefficient of the reaction, and the rate at which the reaction liquid acquired the temperature of 50°.

The temperature coefficient for 30° was 6·03, so correction (*a*) was 1·66 mins.

To determine (*b*) we have $\Delta x_T/\Delta t_T = k_T[\mathrm{H_2O}][\mathrm{CPh_3Cl}]$ where k_T is the velocity coefficient at temperature $T°$, and Δx_T is the small amount of reaction, *i.e.*, increase in the concentration of hydrogen chloride, during the small period of time Δt_T. If $[\mathrm{H_2O}]$ and $[\mathrm{CPh_3Cl}]$ are assumed to be constant, then

$$k_T/k_{50°} = [\Delta x_T/\Delta t_T]/[\Delta x_{50°}/\Delta t_{50°}]$$

Further, if the temperature changes smoothly from 20° to 50° and yet $[\mathrm{H_2O}]$ and $[\mathrm{CPh_3Cl}]$ remain the same at any temperature for which k_T is required over the time interval of about 4 mins. (this approximation is sufficiently correct for the present purpose) then

$$\Sigma_{20°}^{50°}k_T\Delta t_T/\Sigma k_{50°}\Delta t_{50°} = \Sigma_{20°}^{50°}\Delta x_T/\Sigma\Delta x_{50°}$$

and where

$$\Sigma_{20°}^{50°}\Delta x_T = \Sigma\Delta x_{50°}$$

then

$$\Sigma\Delta t_{50°} = \Sigma_{20°}^{50°}k_T\Delta t_T/k_{50°}$$

From the temperature coefficient, the values of k_T between 20° and 50° were calculated for $[\mathrm{H_2O}] = 0·3713$, $[\mathrm{CPh_3Cl}] = 0·1000$, and a curve drawn relating time of immersion to $k_T/k_{50°}$, $T°$ being the temperature reached by the reaction liquid at the corresponding time of immersion. By inspection, a time—$\Sigma\Delta t_{50°} = 1·10$ mins.—was found for which the areas corresponding to $\Sigma_{20°}^{50°}\Delta x_T$ and $\Sigma\Delta x_{50°}$ were equal.

Finally, the corrections (*a*) and (*b*) give a total correction of $t_0 = (1·10—1·66)$ mins. $= -$ 0·56 min.

Details of Experiments on the Forward Reaction.—In Table III are given details of experiments on the forward reaction to illustrate the variation in the values of the velocity coefficients during representative runs; k_1 is the value calculated from the equation for an irreversible second-order reaction and k_1* is that calculated from Baker and Nathan's equation (J., 1936, 236), both being expressed in l. g.-mol.$^{-1}$ min.$^{-1}$. As the two are approximately identical, only two examples are given for the latter coefficient.

TABLE III.

(i) $[\mathrm{H_2O}] = 0·1213$; $[\mathrm{CPh_3Cl}] = 0·2000$.

t.	*x*.	*x* (corr.).	k_1.	k_1*.
7·5	0·0060	0·0039	0·0208	0·0222
12·5	0·0077	0·0058	0·0196	0·0202
22·5	0·0111	0·0097	0·0191	0·0193
42·5	0·0189	0·0185	0·0205	0·0214
92·5	0·0342	0·0358	0·0209	0·0269
142·5	0·0380	0·0400	(0·0158)	0·0250
∞	0·0423	0·0448	—	—

(ii) $[\mathrm{H_2O}] = 0·2213$; $[\mathrm{CPh_3Cl}] = 0·2000$.

t.	*x*.	*x* (corr.).	k_1.	k_1*.
7·5	0·0090	0·0073	0·0206	0·0228
12·5	0·0130	0·0118	0·0216	0·0228
22·5	0·0200	0·0197	0·0216	0·0222
42·5	0·0312	0·0324	0·0203	0·0216
72·5	0·0479	0·0512	0·0208	0·0262
102·5	0·0507	0·0544	(0·0162)	0·0212
∞	0·0610	0·0661	—	—

(iii) $[\mathrm{H_2O}] = 0·3713$; $[\mathrm{CPh_3Cl}] = 0·2000$.

7·5	0·0147	0·0137	0·0248
12·5	0·0206	0·0204	0·0237
17·5	0·0273	0·0279	0·0241
27·5	0·0370	0·0389	0·0224
37·5	0·0480	0·0514	0·0230
47·5	0·0584	0·0630	0·0237
∞	0·0747	0·0815	—

(iv) $[\mathrm{H_2O}] = 0·5213$; $[\mathrm{CPh_3Cl}] = 0·2000$.

5·5	0·0190	0·0186	0·0347
10·5	0·0316	0·0328	0·0344
16·5	0·0470	0·0502	0·0354
24·5	0·0630	0·0682	0·0350
33·5	0·0723	0·0788	(0·0313)
42·5	0·0803	0·0877	(0·0289)
∞	0·0858	0·0940	—

If the coefficients are calculated from Bateman and Hughes's equation (J., 1937, 1187) for a first-order reaction with a second-order reverse reaction, not only are they less consistent in any one run, but they also show a much greater variation with change of water concentration.

Details of Experiments on the Reverse Reaction.—The reverse reaction was too rapid to permit of the determination of the velocity coefficients, k_2, but Table IV gives details of experiments in all of which [CPh_3·OH] = 0·1500 and [H_2O] = 0·5213, *t* again being minutes; in these experiments the time of immersion was taken as t_0.

TABLE IV.

	[HCl] = 0·1000.		[HCl] = 0·1500.		[HCl] = 0·2000.	
t.	[HCl].	[HCl] (corr.).	[HCl].	[HCl] (corr.).	[HCl].	[HCl] (corr.).
4	0·0636	0·0702	0·0918	0·1013	0·1169	0·1292
7	0·0580	0·0647	0·0857	0·0945	0·1151	0·1271
12	0·0560	0·0615	0·0853	0·0940	0·1144	0·1261
17	0·0544	0·0597	0·0848	0·0934	0·1151	0·1271
27	0·0531	0·0583	0·0832	0·0917	0·1147	0·1269
1440	0·0522	0·0572	0·0817	0·0901	0·1137	0·1258
9660	0·0520	0·0570	0·0815	0·0899	0·1138	0·1259

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