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The Coördination Complexes of Mercuric Ion with Cyclohexene

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The formation of compounds from olefins and mercuric salts has been studied very extensively since 1900. Hofmann, Sand and co-workers[1] showed that ethylenic compounds combined with mercuric salts in aqueous solution to yield compounds designated by the formula types I or II.

$$\underset{\text{I}}{>C{=}C<\cdot Hg(OH)X} \qquad \underset{\text{II}}{\begin{matrix} >C-C< \\ | \quad | \\ X\ Hg \quad OH \end{matrix}}$$

Manchot[2] mainly because of the ease of regenerating the olefin from its addition compound claimed that such products are merely molecular compounds and are best represented by formulas of type I. Considerable discussion has appeared in the literature as to the relative validity of the formula types I and II and later investigators[3] on the basis of various sorts of evidence have established the idea that such compounds are formed by real addition to the double bond and are to be represented by formulas of type II.

There have been indications, however, that there may exist coördination compounds of olefins and mercuric salts (type I) in addition to products of type II. Thus, Sand and Breest,[1d] studying the rate of establishment of equilibrium between ethylene, mercuric chloride and ethanol mercuric chloride and not being able to fit the data very well, thought it possible that an equilibrium existed between compounds of the types I and II. Also, Wright[3d] found a serious downward drift in the bimolecular rate constants for the mercuration of several ethylenic compounds. Wright also found that in testing for completeness of the reaction of mercuration of an ethylenic compound, thiocyanate ion would indicate considerable unused mercuric salt when hydroxide ion failed to indicate any. Further, it was found[4] in this Laboratory that isobutene hydrated incompletely in the presence of mercuric nitrate, the residual isobutene being analyzable by bromination and equivalent to the mercuric nitrate.

Recently it was shown by the distribution method that coördination with silver ion[5] is a general property of ethylenic compounds and we have felt that mercuric ion should act analogously to silver ion. We have now investigated by the distribution method possible complex formation between cyclohexene and mercuric ion in aqueous solution and have found that mercuric ion does indeed complex strongly with cyclohexene. In this paper are presented the results of this investigation and some comments on their significance.

Notation.—For the sake of convenience the symbols to be employed together with their definitions are here listed together. The notation used here is as much as possible nearly identical with the notation previously used in connection with the coördination of silver ion with ethylenic compounds.[5b]

B = unsaturated substance, in this case cyclohexene

(Bt) = total concentration of B in the aqueous phase, moles/liter

(B) = concentration of uncomplexed B in the aqueous phase, moles/liter

$(B)_c$ = concentration of B in carbon tetrachloride, moles/liter

(Hg^{++}) = concentration of uncomplexed mercuric ion in the aqueous phase, moles/liter

(Hgt) = total concentration of Hg in aqueous phase, moles/liter

(BHg^{++}) = concentration of the species, BHg^{++} in the aqueous phase, moles/liter

$(BHgOH^{+})$ = concentration of the species, $BHgOH^{+}$ in the aqueous phase, moles/liter

(HNO_3) = concentration of added nitric acid, moles/liter

(H^{+}) = concentration of total acid in the aqueous phase, moles/liter

μ = ionic strength = normality

$K_D = (B)_c/(B)$ = distribution ratio of cyclohexene between carbon tetrachloride and 1 N potassium nitrate = 4305[5b]

$K_E = \dfrac{(Bt) - (B)}{(B)_c[(Hgt) - (Bt) + (B)]}$ = evaluated constant = $\dfrac{(Bt)}{(B)_c[(Hgt) - (Bt)]}$ with negligible error

(1) (a) Hofmann and Sand, *Ber.*, **33**, 1340, 2692 (1900); (b) Sand, *ibid.*, **34**, 1385, 2906 (1901); (c) Sand and Yenssler, *ibid.*, **36**, 3705 (1903); (d) Sand and Breest, *Z. physik. Chem.*, **59**, 424 (1907).

(2) Manchot, *Ber.*, **53**, 984 (1920).

(3) (a) Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922); (b) Sanborn and Marvel, *ibid.*, **48**, 1409 (1926); (c) Griffith and Marvel, *ibid.*, **53**, 789 (1931); (d) Wright, *ibid.*, **57**, 1994 (1935); (e) Hugel and Hibon, *C. A.*, **23**, 3898 (1929); (f) Nesmejanow and Freidina, *Ber.*, **69B**, 1631, 2019 (1936).

(4) Lucas and Eberz, THIS JOURNAL, **56**, 460 (1934).

(5) (a) Eberz, Welge, Yost and Lucas, *ibid.*, **59**, 45 (1937); (b) Winstein and Lucas, *ibid.*, **60**, 836 (1938).

$K_N = \frac{(B \cdot Hg^{++})}{(B)\,(Hg^{++})}$ = coördination constant of mercuric ion for the formation of the complex BHg^{++} (neutral from the acid base standpoint)

$K_B = \frac{(BHgOH^+)(H^+)}{(B)\,(Hg^{++})}$ = coördination constant of mercuric ion for the formation of the basic complex $BHgOH^+$

$K_0 = K_N/K_D$

$K_0' = K_B/K_D$

Procedure and Analysis.—The procedure followed was essentially that described previously in the silver work,[5] with some modifications. Of these, the most important was in the method of preparing the solutions and of taking the samples, so as to eliminate the presence of oxygen. This was a more serious complication than in the silver case, mainly because the presence of oxygen accelerated the separation of some sort of solid organo-mercuric compound. The cyclohexene was distilled from sodium in an atmosphere of nitrogen, weighed into a volumetric flask filled with nitrogen and made up to the mark with carbon tetrachloride. This solution or one diluted with carbon tetrachloride was used for the distributions.

The apparatus for the distribution measurements as shown in Fig. 1 was kept in a thermostat at 25.0 ± 0.03°. The flask, 200 ml., was filled with nitrogen; the materials were pipetted into the flask through the 10-mm. vertical glass tube which usually was kept closed with rubber tubing. A stream of nitrogen, flowing through the stopcock into the atmosphere, was directed into the flask whenever material was introduced into or taken from the flask. The sampling was done with a pipet having a sealed on 3-way stopcock.[4]

There were three stock solutions, *viz.*, (a) 0.286 *M* in mercuric nitrate and 0.142 *N* in added nitric acid, (b) 1 *N* potassium nitrate and (c) 1 *N* nitric acid. Since all three of these have ionic strength $\mu = 1$, solutions of different concentrations, but of same ionic strength, could be obtained easily by mixing.

The mercuric nitrate stock solution was standardized by titration with potassium thiocyanate. The acid concentration (HNO_3) in this solution was found to be 0.147 *N* and not 0.142 *N* as was intended because of nitric acid in the solid mercuric nitrate. The acid concentration was obtained by precipitating the mercury as mercuric sulfide with hydrogen sulfide, and titrating the acid in the filtrate after removal of excess hydrogen sulfide by boiling.

The length of time allowed for the separation of the two phases was much shorter than that allowed in the silver work,[5b] because in this work the concentrations of cyclohexene in the two phases were of the same order of magnitude.

In connection with possible side reactions it was necessary to know how the hydration product of cyclohexene behaved during the bromination procedure. Cyclohexanol, m. p. 22°, purified and distilled, did not react with bromine according to the analytical procedure, in the presence or absence of carbon tetrachloride.

The analytical method has been described previously.[6] In the presence of mercuric ion, the bromate–bromide method of analysis gave satisfactory results with attention to some precautions. It was desirable to allow sufficient time, five minutes, for the initial liberation of bromine and at least five minutes between the addition of sodium chloride and potassium iodide solutions. This time interval could be increased to eleven minutes, without causing differences greater than 0.1%. The excess of bromate–bromide solution could be varied from 15 to 65% without introducing an error greater than ±0.5%. When analyzing the carbon tetrachloride phase, the mercuric ion concentration was made comparable to that in the aqueous phase by the addition of 5 ml. of 0.286 *M* mercuric nitrate.

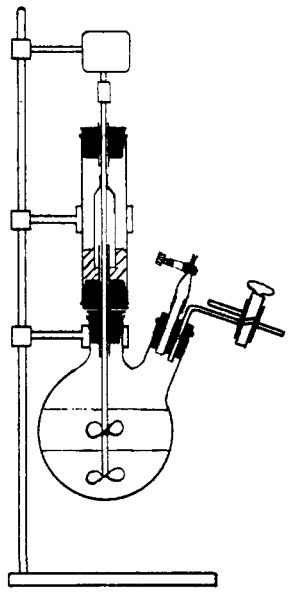


Fig. 1.

The extent to which mercury compounds dissolve in the carbon tetrachloride while cyclohexene is being distributed between carbon tetrachloride and aqueous mercuric nitrate was shown to be less than 0.01 mmol. per liter. This was done by evaporating 50 ml. of the organic phase, after the system had stood for twenty-four hours, taking up the residue (none was visible) in 6 *N* nitric acid, diluting with an equal volume of water, adding saturated hydrogen sulfide solution, and comparing the color with that from known amounts of mercury.

Nature of the Reactions of Cyclohexene in Mercuric Nitrate Solution.—When cyclohexene was distributed between carbon tetrachloride and mercuric nitrate solution containing nitric acid, K_E was much higher than in the case of the silver work[5b] but it varied with time when the acid concentration was low. For about twenty minutes, which seemed to be the time necessary with the present apparatus for establishment of equilibrium between the phases, K_E increased and then it gradually decreased. Thus, when (Hgt) = 0.1907 and (HNO_3) = 0.0980, K_E is 76 at zero time (extrapolated), about 70 after two hours and finally 54 in about twenty hours. At higher acid concentrations this drift seems to be eliminated, K_E varying only as much as would be expected from experimental errors. K_E varies markedly with the acid concentration.

Cyclohexene dissolves readily in aqueous mercuric nitrate. When it does so acid is produced. Under conditions where K_E drifts, there is also a slow further production of acid. These facts are

(6) Lucas and Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

TABLE I

CHANGE IN pH[a] OF MERCURIC NITRATE BY CYCLOHEXENE

(Hgt) Initial	pH	pH with cyclohexene added Initial	After 3 hrs.
0.0954	1.55	1.16	1.04
.1907	1.30	1.07	0.77
.1907	1.19	0.92	0.77[b]

[a] Determined by use of Beckmann pH meter. [b] After two hours.

illustrated in Table I. Under conditions where K_E drifts, the apparent mercury concentration as given by thiocyanate titration decreases with time. Thus, when two ml. of cyclohexene is dissolved in 100 ml. of the 0.286 M mercuric nitrate stock solution, the thiocyanate consumption at the beginning is the theoretical value for all the mercury but it drops a few per cent. per hour at the start and some 27% in thirteen hours. The apparent amount of unsaturation as given by bromination is within experimental error of the theoretical for about one and one-half hours under these conditions and then increases at an accelerating rate so that it is some 3% high after three hours and some 40% high after seventeen hours. In time a solid product separates. When cyclohexene dissolves in mercuric nitrate solution, the odor of cyclohexene is not apparent but it becomes so as thiocyanate is added.

The ready solubility of cyclohexene in aqueous mercuric nitrate with loss of cyclohexene odor, the initial production of acid, the initial theoretical consumption of thiocyanate ion, and the variation of K_E with acid concentration in the distribution measurements indicate the rapid coördination of cyclohexene with mercuric ion to give some sort of compound of the formula type I mentioned previously, accompanied by the production of acid. The secondary effects observed at the lower acid concentrations such as the decrease in apparent mercury concentration, the drift of K_E with time, the further production of acid, the increase in the apparent unsaturation after a time, and the separation of a solid indicate that secondary reactions, not as yet completely understood, are taking place. One of the secondary reactions would seem to be the production of a compound of the formula type II. This would produce acid and decrease the consumption of thiocyanate since compounds of type II consume only half as much thiocyanate as mercuric ion does.[3d] These secondary reactions were not investigated further because our chief interest at this time was the study of the coördination type of reaction involving mercuric ion.

At higher acid concentrations, K_E is evaluated easily because the coördination process proceeds with essentially no side reactions. At the lower concentrations a simple extrapolation is sufficient to give K_E quite accurately since the secondary reactions are relatively slow.

Equilibria and Equilibrium Constants.—Distributions were made under conditions in which the concentrations of cyclohexene, mercuric nitrate and nitric acid were changed. The data are summarized in Table II. In each case three independent distributions were made, in duplicate, and the stirring times were 0.5, 1.0 and 1.5 hours, respectively. The evaluated constant K_E for each condition was obtained by averaging the three values of K_E or by extrapolating to zero time when there was a systematic decrease of K_E with time.

TABLE II

VALUES OF K_E OBTAINED BY DISTRIBUTION AT 25° OF CYCLOHEXENE BETWEEN CCl_4 AND $Hg(NO_3)_2 + HNO_3 + KNO_3$ AQ. AT $\mu = 1$

(Hgt)	Extrapolated $(B)_c$	(Bt)	(HNO_3)	K_E 0.5 hr.	1 hr.	1.5 hr.	Extrap.
0.0477	0.0320	0.0271	0.2731	41.4	41.6	40.6	41.2
.0954	.0135	.0558	.0490	108.5	105.8	103.2	111.2
.0954	.0153	.0529	.0963	83.6	81.2	79.5	85.6
.0954	.0209	.0449	.2740	42.4	42.2	42.5	42.4
.0954	.00805	.0256	.2740	45.6	44.5	46.5	45.5
.0954	.00364	.0137	.2740	45.0	46.3	46.5	45.9
.0954	.0252	.0376	.5490	24.9	25.8	26.3	25.7
.1907	.0158	.1040	.0980	74.4	72.5	71.0	76.0
.1907	.01001	.0606	.2756	45.5	47.7	47.4	46.8

K_E is relatively insensitive to changes in (Hgt) and $(B)_c$ indicating the formation of a complex ion from one molecule of cyclohexene and one mercuric ion. The large variation of K_E with (HNO_3) speaks against the description of the coördination process by equation 1, which one would write

$$C_6H_{10} + Hg^{++} \overset{K_N}{\rightleftharpoons} C_6H_{10}Hg^{++} \quad (1)$$

$$C_6H_{10} + Hg^{++} + HOH \overset{K_B}{\rightleftharpoons} C_6H_{10}HgOH^+ + H^+ \quad (2)$$

on the basis of strict analogy between mercuric and silver[5] ions. If reaction 1 were the only one to be considered, K_E would equal K_0 and no variation with (HNO_3) would be observed. Reaction 2 suggests itself as being very important.

If we assume that the reaction of cyclohexene with mercuric ion proceeds entirely in the sense of equation 2, the total acid concentration (H^+) is given, with negligible error, by equation 3 as the sum of the acid present in

$$(H^+) = (HNO_3) + (Bt) \quad (3)$$

the mercuric nitrate solution and that produced by reaction 2. Also, according to equation 4,

K_0' the product of (H^+) and K_E, should be a constant. The values of K_0' which are obtained in

$$K' = K_B/K_D = (H^+)\,K_E = \frac{(BHgOH^+)(H^+)}{(B)_c(Hg^{++})} \quad (4)$$

this way are given in the last column of Table III. K_0' is seen to be reasonably constant, varying only between 11.7 and 15.7, with 13.7 ± 1.2 as the mean value. The conclusion can be drawn, therefore, that the reaction between cyclohexene and mercuric ion proceeds predominantly in the sense of equation 2 to produce a complex ion $C_6H_{10}\cdot HgOH^+$.

TABLE III

VALUES OF K_0' USING EQUATIONS 3 AND 4

(Hgt)	$(B)_c$	(Bt)	K_E	(HNO_3)	$(H^+) = (Bt) + (HNO_3)$	$K_0' = (H^+)K_E$
0.0477	0.0320	0.0271	41.2	0.2731	0.3002	12.4
.0954	.0135	.0558	111.2	.0490	.1048	11.7
.0954	.0153	.0529	85.6	.0963	.1492	12.8
.0954	.0209	.0449	42.4	.2740	.3189	13.5
.0954	.00805	.0256	45.5	.2740	.2996	13.5
.0954	.00304	.0137	45.9	.2740	.2877	13.0
.0954	.0252	.0376	25.7	.5490	.5866	15.1
.1907	.0158	.1040	76.0	.0980	.2020	15.4
.1907	.01001	.0606	46.8	.2756	.3362	15.7
					Mean	13.7
					Mean deviation	±1.2

On the assumption that reaction proceeds according to both equations 1 and 2 the data can be correlated somewhat better than on the basis of only the one reaction. From equation 5

$$K_E = \frac{(BHg^{++}) + (BHgOH^+)}{(B)_c(Hg^{++})} \quad (5)$$

and the definitions of K_0 and K_0', the relation between K_E, K_0, K_0' and (H^+) is given by equation 6.

$$K_E = K_0 + K_0'/(H^+) \quad (6)$$

A first approximation to K_0 can be obtained from the series of runs in which (Hgt) = 0.0954 by plotting K_E against $1/(H^+)$, using (H^+) from Table III. The first approximation was five. Then this value of K_0 was used to obtain a better approximation to the total acid concentration with the relation shown in equation 7

$$(H^+) = (HNO_3) + (Bt)(K_E - K_0)/K_E \quad (7)$$

where $(K_E - K_0)/K_E$ represents the fraction of (Bt) in the form of $(BHgOH^+)$. When K_E was plotted against the corrected (H^+) as shown in Fig. 2, the value of K_0 by this second approximation was five also.

On recalculating K_0' by means of equation 6 using the corrected (H^+) values and the value of $K_0 = 5$, K_0' varies only from 10.9 to 11.9 (Table IV) with 11.6 ± 0.3 as the mean value. The agreement is even better, if the result at the very lowest acid concentration is neglected.

TABLE IV

CORRECTED K_0' VALUES, WITH (Hgt) = 0.0954, $K_0 = 5$ USING EQUATION 6

$(B)_c$	(Bt)	K_E	(HNO_3)	(H^+) equation 7	$K_0' = (K_E-5)(H^+)$
0.0135	0.0558	111.2	0.0490	0.1023	10.9
.0153	.0529	85.6	.0963	.1461	11.8
.0209	.0449	42.4	.2740	.3136	11.7
.00805	.0256	45.5	.2740	.2968	11.9
.00304	.0137	45.9	.2740	.2862	11.7
.0252	.0376	25.7	.5490	.5793	11.8
				Mean	11.6
				Mean deviation	±0.3

From the data of Table IV it can be concluded that when mercuric ion coördinates with cyclohexene, there are two one-to-one complexes formed, *viz.*, $C_6H_{10}Hg^{++}$ and $C_6H_{10}HgOH^+$. The respective equilibrium constants, $K_N = K_0K_D$ and $K_B = K_0'K_D$ are 2.2×10^4 and 5.0×10^4, respectively, when (Hgt) is approximately 0.1 *M*.

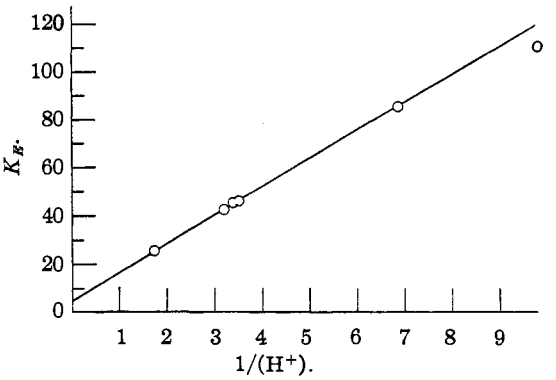


Fig. 2.—Change of K_E with $1/(H^+)$ at (Hgt) = 0.0954 *M*. (H^+) is obtained from equation 7.

There would appear to be a drift in K_0' as (Hgt) is varied. If the assumption is made that K_0 does not change, then K_0' as calculated from equations 6 and 7 varies with (Hgt) as shown in Table V. K_0 may and probably does change somewhat with (Hgt) but since it is so small compared to $(K_E - K_D)$, such a variation can hardly affect very much the trend in K_0' in Table V.

TABLE V

EFFECT OF CHANGE IN (Hgt) ON K_0', WHEN $K_0 = 5$

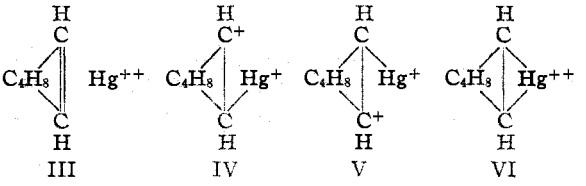
(Hgt)	$K_0' = (H^+)(K_E-5)$
0.0477	10.6
.0954	11.6[a]
.1907	13.7[b]

[a] Average K_0' value, Table IV. [b] Average of two values, 13.8 and 13.6.

A similar but somewhat smaller trend in the constant with the proportion of the various salts making up the total ionic strength of unity was

observed previously in the olefin–silver work.[5] These trends must be due to the fact that even though in the silver work the ionic strength was kept at unity and in the present work it was kept at unity except for changes due to reaction 2, the activity coefficients of the various ionic species change as silver or mercuric nitrate is substituted for potassium nitrate or nitric acid.

Structures.—The coördination complexes of mercuric ion with cyclohexene can be formulated much like the silver–olefin[5] or the positive bromo-olefin complexes.[7] The resonating forms of the cyclohexenemercurinium ion[8] can be represented as III, IV, V and VI and the cyclohexenemercur-



III IV V VI

inium hydroxide ion $C_6H_{10}\cdot HgOH^+$ can be represented similarly with the difference that the mercury atom holds one hydroxyl radical.

The values of K_B and K_N which have been obtained indicate the very extensive hydrolysis of the species $C_6H_{10}Hg^{++}$. In fact, the value for the ionization constant of the base $C_6H_{10}\cdot HgOH^+$ which is given by K_B and K_N is approximately 5×10^{-15}. One would rather expect a low value for the ionization constant of this base, especially if structure VI is at all important, for this form involves an increase in the effective charge on the mercury atom and a consequent decrease in the strength of the corresponding base.

Significance of Mercurinium Complexes.—From a theoretical point of view these coördination complexes of mercury are of great importance. They may be regarded as typical examples of the rather large group of poorly defined substances which are recognized as intermediates in chemical changes, but which usually cannot be isolated.

The process of mercuration of an olefin with production of stable reaction products would appear to be analogous to the *trans* addition of bromine or of bromine derivatives to the double bond. Negative ions or various solvent molecules can attack the substituted ethylenebromonium ions to give dibromides, bromohydrins, etc.[7] Just so are the substituted ethylenemercurinium ions thought to give compounds of the formula type II. One difference is that the mercury complex is so much less reactive that it can be studied directly. In reactivity the mercury complexes would appear to be intermediate between the silver ion and positive bromine analogs. Because of the analogy between bromination and mercuration, we would expect *trans* addition in mercuration also. Actually the mode of addition is uncertain but there is plenty of evidence that mercuration does not proceed by two concurrent reactions, *i. e.*, *cis* addition and *trans* addition[3] to the double bond.

Solid mercury–olefin coördination complexes, comparable to the known solid silver–olefin coördination complexes,[5b] would be expected to exist. It may be that some of the products which have been obtained by workers in the past were actually of the coördination type.

With the finding of coördination complexes of an olefin and mercuric ion the state of the reaction of mercuration has been somewhat complicated. It is known that the mercuration reaction proceeds in some cases to a measurable equilibrium.[1d,3d] Now it would appear that equilibria between the olefin, mercuric salt, compound of type I and compound of type II are involved. In many reactions of mercurated olefins it remains to be seen to what extent these equilibria play a role.

(7) (a) Roberts and Kimball, THIS JOURNAL, **59**, 947 (1937); (b) Winstein and Lucas, *ibid.*, **61**, 1576 (1939).

(8) The similarly constituted complex, $C_2H_4Br^+$, has been named the ethylenebromonium ion; Winstein and Lucas, *ibid.*, **61**, 2845 (1939).

Summary

Coördination complexes of mercuric ion with cyclohexene have been studied chiefly by the distribution of cyclohexene between carbon tetrachloride and aqueous solutions containing mercuric nitrate, nitric acid and potassium nitrate at ionic strength of $\mu = 1$.

The data indicate that two rapid reactions take place: $C_6H_{10} + Hg^{++} \rightleftarrows C_6H_{10}Hg^{++}$ and $C_6H_{10} + Hg^{++} + H_2O \rightleftarrows C_6H_{10}HgOH^+ + H^+$. The equilibrium constant K_N for the first reaction is 2.2×10^4 and K_B, for the second reaction, is 5.0×10^4.

Secondary slower reactions proceed concurrently with the other two.

The significance of mercury–olefin complexes for mercuration phenomena is discussed briefly.

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