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# Effect of temperature and hydrochloric acid on the ultrasonic degradation of poly acrylic acid in aqueous solutions

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**Abstract :** The ultrasonic degradation of poly acrylic acid was carried out in water and aqueous hydrogen chloride solutions. Some of kinetics models are used to obtain of rate constants. The calculated rate constants reveals that rate of degradation were decreased by increasing temperature and decreasing ultrasound power. Also the effect of hydrochloric acid on the rate of degradation was interpreted in terms of absolute viscosity and intrinsic viscosity of polymer. The rate of degradation slightly was affected by concentration of hydrochloric acid. By adding hydrochloric acid the absolute viscosity and intrinsic viscosity of poly acrylic acid decreased. A reduction in the first factor accelerates the rate of degradation; whereas the second factor reduces the rate of

degradation. By adding hydrochloric acid the ionization of ionizable groups were suppressed; therefore, the chains of poly acrylic acid shrinks and the end-to-end distance of polymer chains become smaller by adding hydrochloric acid in poly acrylic acid solutions; therefore, strain rate were reduced and the degradation rate decreases too. By considering that, the two mentioned factors have the opposite effect on the rate of degradation, consequently the rate of degradation do not affected by adding hydrochloric acid in poly acrylic acid solutions. © Global Scientific Inc.

**Keywords :** Modeling; Degradation; Polyelectrolyte; Kinetic.

## INTRODUCTION

Poly acrylic acid (PAA) is a water soluble polymer, which has various applications in industry. The degradation of polymers can occur because of heat, light, chemical reagents or ultrasonic radiation<sup>[1]</sup>. Degradation of PAA were studied by various methods such as thermal degradation<sup>[2-5]</sup>, chemical degradation<sup>[6]</sup>, enzymatic degradation<sup>[7]</sup> and ultrasonic degradation<sup>[8,9]</sup>. The ultrasonic degradation process has several unique fea-

tures that distinguish it from others degradation, such as a non-random nature and molecular weight dependence<sup>[10]</sup>. The scission of polymer chains in a solution occurs preferentially near the middle of the chain<sup>[11,12]</sup>. Ultrasonication has subsequently proved to be a highly advantageous method for degrading macromolecules because it reduces their molecular weight simply by splitting the most susceptible chemical bond in the center of the chain without causing any changes in the chemical nature of the polymer<sup>[13]</sup>. The ultrasound waves do

not directly interact with polymer chains during sonication of polymer solutions. The main effects of sonication are because of cavitation phenomena<sup>[11]</sup>. Formation, growth and rapid collapse of microscopic bubbles cause the movement of the solvent molecules around the bubbles. These movements set up large shear fields that are primarily responsible for the degradation of polymer<sup>[11,14,15]</sup>. Some kinetic models are proposed for treatment of rate of ultrasonic degradation. In this research applicability of kinetic models are examined for ultrasonic degradation of PAA in aqueous solution of hydrogen chloride.

## EXPERIMENTAL

### Materials

Poly(acrylic acid), PAA, with a viscosity average molecular weight,  $M_v$ , of 450 000 (Aldrich) was used without further purification. Hydrochloric acid was supplied by Merck. Double distilled water was used for preparation of solutions.

### Apparatus and procedure

PAA solution ( $5 \text{ g}\cdot\text{L}^{-1}$ ) was prepared gravimetrically by an analytical balance (Sartorius CP224 S) with a precision of  $\pm 1 \times 10^{-4} \text{ g}$ . Ultrasonic degradation was performed in water and two aqueous solutions of hy-

drogen chloride (0.001 and 0.1 M) at four temperatures. For the degradation,  $50 \text{ cm}^3$  polymer solutions was placed in the jacket flask, and its temperature was controlled within  $\pm 0.5^\circ\text{C}$  by circulating thermostated water and sonication has been continued for a time which molecular weight tends to have a constant value. An ultrasonic generator (Dr. Hielscher UP400 S ultrasonic processor) with an H3 sonotrode with diameter 3 mm was used in this experiment. The frequency of the ultrasound was 24 kHz. Periodically, samples of the sonicated solution were removed and their molecular weights were measured using gel permeation chromatography.

## RESULTS AND DISCUSSION

Sonication of PAA solutions were carried out in water and two aqueous solutions of hydrogen chloride (0.001 and 0.1 M) at various temperatures and ultrasound power. For example the relationships between  $M_n$  and sonication time are presented in Figure 1. From these findings, it is clear that  $M_n$  decreases with sonication time and tends to have a constant value (limiting molecular weight). The limiting molecular weights were increased by increasing temperature and decreasing ultrasound power. However the limiting molecular weights don't show meaningful relation with HCl concentration.

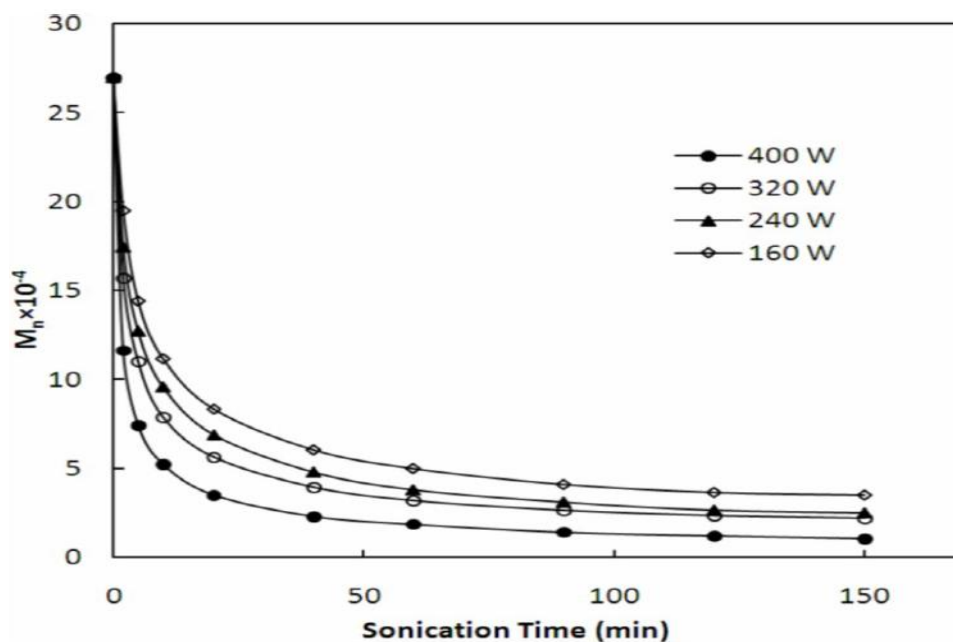


Figure 1 : Relation molecular weight versus sonication time for PAA in aqueous solution at 298.15 K and various ultrasound power.

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To evaluating the ability of proposed models in kinetics of ultrasonic degradation of polymers for prediction rate constant in examined systems, various models were used. Therefore, Mehrdad, Schmid, El'tsefon-Berlin, Tang-Liu, Madras, Malhotra, Ovenall and Giz models were used to evaluating rate constant of degradation.

Schmid proposed an equation to relating molecular weight to the sonication time. The integral form of Schmid's model is<sup>[10,16]</sup>

$$M_{lim}(M_0^{-1} - M_t^{-1}) + \ln\left(\frac{M_{lim}^{-1} - M_0^{-1}}{M_{lim}^{-1} - M_t^{-1}}\right) = k_s \left(\frac{M_{lim}^2}{Cm_0^2}\right)t \quad (1)$$

where  $M_{lim}$ ,  $M_0$  and  $M_t$  are limiting molecular weight, initial molecular weight and molecular weight at time, respectively. A plot of the left hand side of the equation versus time yields a straight line. The rate constant is calculated from its slope. Here the polymer concentration,  $C$ , is written explicitly to give the dependence of scission rate on concentration. The obtained rate constants of this model,  $k_s$ , and correlation coefficients,  $r$ , are listed in TABLE 1. The correlation coefficient is defined as

$$r^2 = \frac{(\sum(x_i - \bar{x})(y_i - \bar{y}))^2}{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2} \quad (2)$$

where  $x$  and  $y$  are denote time and left hand side of the Equation (1), respectively.

Malhotra proposed that in ultrasonic degradation of polymer, the time dependence of the molecular weight is given by<sup>[17,18]</sup>:

$$M_t^{-1} - M_0^{-1} = k_M t \quad (3)$$

A plot of the left hand side of the equation versus time yields a straight line which its slope is rate constant. The lack of a limiting molecular weight is failure of this model. The rate constants of this model,  $k_M$ , and correlation coefficients,  $r$ , are listed in TABLE 2.

Tang and Liu are proposed a kinetic equation by considering ultrasonic degradation process as second order reaction<sup>[19]</sup>

$$(M_t - M_{lim})^{-1} - (M_0 - M_{lim})^{-1} = k_T t \quad (4)$$

The degradation rate constant,  $k_T$ , can be found as the slope of the line from a plot of the left hand side of the equation versus time. The rate constants of this model,  $k_T$ , and correlation coefficients,  $r$ , are listed in TABLE 3.

**TABLE 1 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases Schmid model.**

T (K)	USP (W)	$k_s \times 10^6$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	1.28	1.51	1.95	0.945	0.986	0.831
298.15	400	1.30	1.30	1.22	0.919	0.991	0.873
303.15	400	1.03	1.19	1.12	0.948	0.981	0.871
308.15	400	0.853	0.944	0.993	0.945	0.990	0.893
298.15	320	0.473	0.819	0.449	0.953	0.985	0.932
298.15	240	0.335	0.540	0.263	0.930	0.989	0.938
298.15	160	0.208	0.388	0.194	0.941	0.969	0.929

**TABLE 2 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases Malhotra model.**

T (K)	USP (W)	$k_M \times 10^7$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	7.90	7.28	10.94	0.910	0.693	0.989
298.15	400	8.11	6.62	8.44	0.931	0.676	0.973
303.15	400	6.92	6.32	8.08	0.915	0.710	0.970
308.15	400	6.07	5.77	7.73	0.894	0.703	0.971
298.15	320	4.31	4.52	4.87	0.894	0.788	0.943
298.15	240	3.56	3.50	3.39	0.932	0.840	0.928
298.15	160	2.59	2.52	2.78	0.908	0.743	0.926

TABLE 3 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases Tang model.

T (K)	USP (W)	$k_T \times 10^6$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	2.70	5.42	2.21	0.956	0.930	0.926
298.15	400	2.52	5.22	1.88	0.940	0.955	0.942
303.15	400	2.51	4.84	1.79	0.953	0.911	0.941
308.15	400	2.49	3.93	1.62	0.935	0.954	0.960
298.15	320	1.95	3.43	1.38	0.937	0.945	0.960
298.15	240	1.57	2.37	1.08	0.915	0.973	0.952
298.15	160	1.40	2.42	0.98	0.902	0.927	0.932

El'tsefon and Berlin on the basis of their work with polystyrene solutions in benzene, have suggested that the molecular weight with the sonication time as follow<sup>[12,20]</sup>:

$$M_t^{-2} - M_0^{-2} = \beta k_e t \quad (5)$$

where  $\beta$  is a constant accounting for the polydispersity of the polymer so that the rate constant can be found as the slope of the left hand side of the equation versus time. This model also lacks a limit molecular weight. By considering  $\beta = 1$ , the rate constants of this model,  $k_e$ , and correlation coefficients,  $r$ , are listed in TABLE 4.

A model proposed by Ovenall and co-workers as an approximate description of the degradation process gives the time dependence of the molecular weight during sonication by<sup>[12,21]</sup>:

$$\ln\left(\frac{M_{lim}^{-1} - M_0^{-1}}{M_{lim}^{-1} - M_t^{-1}}\right) = k_o \left(\frac{M_{lim}}{Cm_0}\right) t \quad (6)$$

So that the plot of the left hand side of the equation versus time produces a linear relationship, the slope of which yields the rate constant. Here the polymer concentration is written explicitly to give the dependence of scission rate on concentration. The rate constants of this model,  $k_o$ , and correlation coefficients,  $r$ , are listed in TABLE 5.

Madras and co-workers have proposed a model that takes the continuous distribution kinetics into account<sup>[22-24]</sup>. The time dependence of the average molecular weight in this model is same as in the Ovenall model.

$$\ln\left(\frac{M_{lim}^{-1} - M_0^{-1}}{M_{lim}^{-1} - M_t^{-1}}\right) = k_{Ma} M_{lim} t \quad (7)$$

The rate constants of this model,  $k_{Ma}$ , and correlation coefficients are listed in TABLE 6.

Mehrdad proposed an equation relating the rate of scission to the molecular weight<sup>[24]</sup>.

$$-\frac{dM}{dt} = k_{Mc} M(M - M_{lim})^\beta \quad (8)$$

The integral form of Mehrdad's model is<sup>[25-27]</sup>:

$$M_t^{-\beta} {}_2F_1(\beta, \beta, 1 + \beta, M_{lim}/M_t) - M_0^{-\beta} {}_2F_1(\beta, \beta, 1 + \beta, M_{lim}/M_0) = \beta k_{Mc} t \quad (9)$$

where  ${}_2F_1$  is Hypergeometric function which is given by<sup>[28]</sup>:

$${}_2F_1(a, b, c, x) = \sum_{n=0}^{\infty} \frac{(a+n-1)!(b+n-1)!(c-1)!}{(c+n-1)!(a-1)!(b-1)!(c)_n} \frac{x^n}{n!} \quad (10)$$

A plot of the left hand side of the equation versus time yields a straight line. The rate constant is calculated from its slope. This model is fitted to experimental data and the best value of  $\beta$  is found to be 1, 1.2 and 1 for degradation in water, hydrogen chloride 0.001 M and 0.1 M, respectively. The obtained rate constants of this model,  $k_{Mc}$ , and correlation coefficients,  $r$ , are listed in TABLE 7. When  $\beta=1$ , Mehrdad's model is same as the Madras model.

Giz and co-workers were suggested that the average molecular weight evolution could be approximated as<sup>[29,30]</sup>:

$$\ln\left(\frac{M_{lim} - M_0}{M_{lim} - M_t}\right) = (k_c t)^\beta \quad (11)$$

where  $\beta$  is a measure of the heterogeneity of the process and left as a fit parameter. This model is fitted to experimental data and the best value of  $\beta$  is found to be 0.45, 0.42 and 0.45 for degradation in water, hydrogen chloride 0.001 M and 0.1 M, respectively. The rate constants of this model,  $k_c$ , and correlation coefficients,  $r$ , are listed in TABLE 8. For comparison efficiency of the used models, the mean correla-

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tion coefficients of all models are listed in TABLE 9. The result of kinetics treatment reveal that applicability of models for studied system are satisfactory

expect Malhotra's model. Drawback of Malhotra's model may be arising from the lack of a limiting molecular weight.

**TABLE 4 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases El'tsefon model.**

T (K)	USP (W)	$k_E \times 10^{11}$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	4.78	3.95	9.52	0.997	0.960	0.897
298.15	400	5.07	3.30	5.65	0.988	0.944	0.942
303.15	400	3.74	3.05	5.21	0.997	0.966	0.941
308.15	400	2.92	2.57	4.77	0.999	0.959	0.950
298.15	320	1.56	2.32	1.99	0.999	0.971	0.988
298.15	240	1.13	1.67	1.04	0.997	0.978	0.994
298.15	160	0.64	1.06	0.73	1.000	0.984	0.993

**TABLE 5 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases Overall model.**

T (K)	USP (W)	$k_O \times 10^4$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	4.89	5.96	5.42	0.995	0.979	0.978
298.15	400	4.83	5.57	4.41	0.993	0.972	0.987
303.15	400	4.39	5.23	4.18	0.997	0.984	0.984
308.15	400	4.04	4.62	3.91	0.995	0.975	0.990
298.15	320	2.99	4.25	2.82	0.996	0.979	0.988
298.15	240	2.45	3.34	2.07	0.996	0.979	0.991
298.15	160	1.93	2.85	1.77	0.995	0.994	0.988

**TABLE 6 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases Madras model.**

T (K)	USP (W)	$k_{Ma} \times 10^6$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	1.36	1.66	1.51	0.995	0.979	0.978
298.15	400	1.34	1.55	1.22	0.993	0.972	0.987
303.15	400	1.22	1.45	1.16	0.997	0.984	0.984
308.15	400	1.12	1.28	1.09	0.995	0.975	0.990
298.15	320	0.831	1.18	0.784	0.996	0.979	0.988
298.15	240	0.682	0.927	0.575	0.996	0.979	0.991
298.15	160	0.537	0.791	0.491	0.995	0.994	0.988

**TABLE 7 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases Mehrdad model.**

T (K)	USP (W)	$k_{Me} \times 10^6$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	1.36	0.311	1.51	0.995	0.998	0.978
298.15	400	1.34	0.287	1.22	0.993	0.998	0.987
303.15	400	1.22	0.267	1.16	0.997	0.995	0.984
308.15	400	1.12	0.229	1.09	0.995	0.999	0.990
298.15	320	0.830	0.206	0.783	0.996	0.998	0.994
298.15	240	0.681	0.153	0.574	0.996	0.999	0.991
298.15	160	0.538	0.130	0.490	0.995	0.992	0.988

TABLE 8 : The rate constant of ultrasonic degradation of poly(acrylic acid) in various conditions on the bases Giz model.

T (K)	USP (W)	$k_G \times 10^4$			$r^2$		
		Water	[HCl]=0.001 M	[HCl]=0.1 M	Water	[HCl]=0.001 M	[HCl]=0.1 M
293.15	400	2.99	5.19	2.57	0.995	0.994	0.992
298.15	400	2.77	5.11	2.34	0.992	0.993	0.992
303.15	400	2.75	4.82	2.27	0.997	0.996	0.990
308.15	400	2.70	4.35	2.14	0.997	0.996	0.993
298.15	320	2.29	4.01	1.89	0.988	0.998	0.998
298.15	240	1.96	3.22	1.56	0.996	0.999	0.994
298.15	160	1.76	3.13	1.51	0.977	0.989	0.975

TABLE 9 : The mean correlation coefficient,  $\bar{r}^2$  of the used models

Model	Mehrdad	Schmid	Malhotra	Tang	El'tsefon	Ovenall	Madras	Giz
$\bar{r}^2$	0.993	0.940	0.868	0.940	0.974	0.987	0.987	0.992

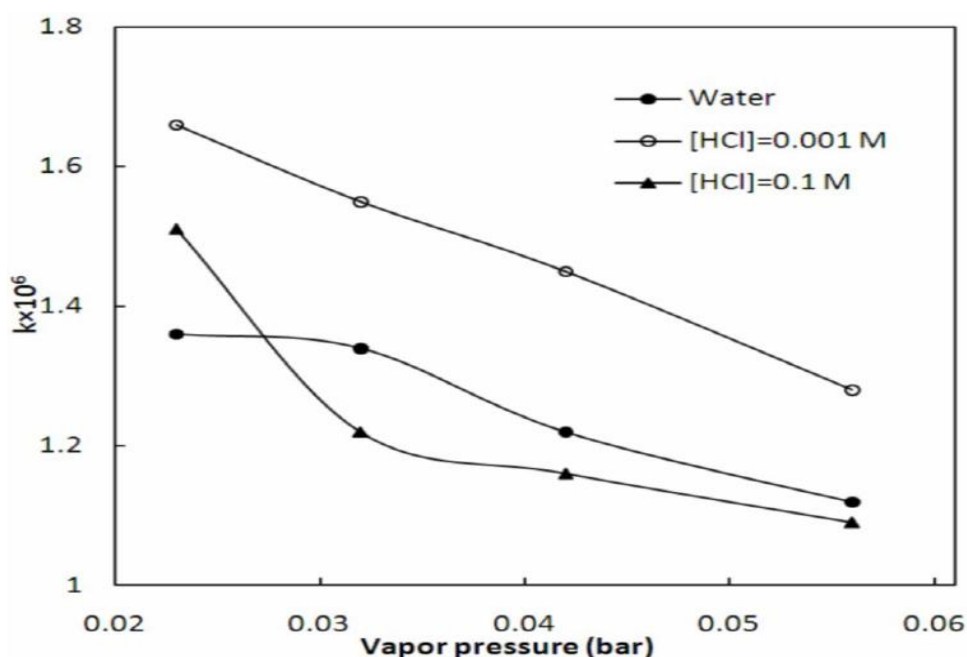


Figure 2 : Relation rate constant versus solvent vapor pressure.

The obtained values of  $k$  indicate that the rates of degradation were increased by increasing ultrasound power. This might be because of, with increasing ultrasound power a large number of cavitation bubbles per unit volume of solution increases, so that rate of degradation was increased. Additionally with increasing ultrasound power the radius of cavitation bubbles increases, therefore higher shear force generated during collapsing bubbles. The obtained results indicate that the rate of degradation was decreased by increasing temperature. This might be because of, with increasing temperature the vapor pressure of solvent increases and this causes a reduction in collapsing shock because of a

cushioning effect; therefore, the extent of degradation is reduced<sup>[31,32]</sup>. The relationship between rate constants of Madras's model and vapor pressure of solvent are illustrate in Figure 2. However the Vagner equation has been used in estimating vapor pressure of water<sup>[33]</sup>.

With adding hydrochloric acid in PAA solutions, two solution factors, the absolute viscosity and intrinsic viscosity, decreased. A reduction in the first factor accelerates the rate of degradation. By adding hydrochloric acid in PAA solutions the ionization of ionizable groups were suppressed and hydrodynamic volume of polyelectrolyte's chains were decreased, this leads to a reduction in intrinsic viscosity. The intrinsic viscosities

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of PAA in water, hydrogen chloride 0.001 M and 0.1 M at 298.15 K are 8.56, 0.397 and 0.0927 m<sup>3</sup>kg<sup>-1</sup>, respectively<sup>[34]</sup>. The intrinsic viscosities were measured using a jacketed Ubbelohde viscometer with 0.4 mm capillary. On the other hand, the end-to-end distance of polymer chains is related to the intrinsic viscosity. Therefore, the chains of PAA shrinks and the end-to-end distance of polymer chains become smaller by adding hydrochloric acid in PAA solutions; therefore, strain rate were reduced and the degradation rate decreases too. By considering that, the two mentioned factors have the opposite effect on the rate of degradation, consequently the rate of degradation do not affected by adding hydrochloric acid in PAA solutions.

## CONCLUSIONS

The ultrasonic degradation of PAA solutions was carried in water and two aqueous solutions of hydrogen chloride (0.001 and 0.1 M) at various temperatures and ultrasound power. Some of kinetics models were used for treatment of kinetics of degradation. The result of kinetics treatment reveal that applicability of models for studied system are satisfactory expect Malhotra's model.

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