

## Stoichiometric Solvation Effects. Solvolysis of Trifluoromethanesulfonyl Chloride

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Solvolyse of trifluoromethanesulfonyl chloride (TFMSC) in water and in aqueous binary mixtures of acetone, ethanol and methanol are investigated at 25, 35 and 45 °C. The Grunwald-Winstein plot of first-order rate constants for the solvolytic reaction of TFMSC with  $Y_{Cl}$  (based on 2-adamantyl chloride) shows marked dispersions into three separate curves for three aqueous mixtures. The extended Grunwald-Winstein plots for the solvolysis of TFMSC show better correlation. The large negative  $\Delta S^\ddagger$  and relatively small positive  $\Delta H^\ddagger$  reveals that the solvolytic reaction proceeds *via* a typical bimolecular reaction mechanism. The  $l$  and  $m$  values determined in various solvents are consistent with the proposed mechanism of the general base catalysis  $S_A N/ S_N 2$  reaction mechanism for TFMSC solvolyses based on mass law and stoichiometric solvation effect studies.

**Key Words :** Dispersion, Stoichiometric solvation effects, Kinetic solvent isotopic effects

### Introduction

Aromatic sulfonyl halides are known to solvolyze by a borderline mechanism<sup>1</sup> as in the solvolysis of benzyl chloride.<sup>2</sup> There has been, however, much dispute over the mechanism as to whether it is an  $S_N 2^3$  or an  $S_A N^4$  process, the former being preferred lately. A particularly important system which contains tetracoordinate sulfur is  $ArSO_2Cl$ ; aromatic sulfonyl chlorides are important reagents in organic synthesis and substitution reactions of these compounds bridge inorganic and organic chemistry.

Linear free energy relationships (LFER) and solvent effects in the solvolyses of sulfonyl halides, especially substituted benzenesulfonyl chlorides, have received much experimental attention,<sup>5</sup> but little work has been done on the solvent stoichiometric effect on alcohol-water mixed solvents, especially for the solvolyses of aliphatic sulfonyl halides.

In order to examine the quantitative solvent effects, it is necessary to take into account the LFER and the stoichiometric solvation effects based on a third order reaction mechanism.

Dispersion into separate lines or curves in the correlation of the specific rates of solvolysis of a substrate in various binary mixtures was documented<sup>6</sup> in early treatment using the Grunwald-Winstein eqn. (1).<sup>7</sup>

$$\log(k/k_o) = mY + c \quad (1)$$

In eqn. (1),  $k$  is the rate constant for solvolysis in any solvent relative to 80% ethanol-water ( $k_o$ ),  $m$  is the sensitivity of the substrate to ionizing power ( $Y$ ) and  $c$  is a residual intercept term.

In general, dispersion effects in unimolecular solvolysis<sup>8</sup> make smaller contribution to the overall LFER than solvent nucleophilicity effects in bimolecular solvolysis.<sup>6a,b,c,8c</sup> It

was suggested that a second term which is governed by the sensitivity  $l$  to solvent nucleophilicity  $N_T$ ,<sup>9,10</sup> should be added to eqn. (1) for bimolecular solvolysis.<sup>8c</sup> The resulting eqn. (2) is often referred to as the extended Grunwald-Winstein equation.<sup>8c</sup>

$$\log(k/k_o) = mY + lN_T + c \quad (2)$$

For solvolyses in alcohol-water mixtures, interpretations based on a third order reaction mechanism are more complex, but significant new information is available because two products are formed. Thus there are four possible third order rate constants in the solvolysis reaction,  $k_{aa}$ ,  $k_{aw}$ ,  $k_{wa}$ , and  $k_{ww}$ .<sup>6g,11</sup>

In this study, we determined pseudo first order rate constants for solvolyses of trifluoromethanesulfonyl chloride (TFMSC) with a strong electron withdrawing group in alcohol-water mixtures, and application of the extended Grunwald-Winstein equation and also estimated third order constants,  $k_{ww}$  ( $k_{wa} + k_{aw}$ ) and  $k_{aa}$ . We discuss the mechanism of solvolytic reaction of TFMSC using  $l/m$ , third order rate constants and kinetic solvent isotope effects.

### Results and Discussion

The rate constants for solvolyses of TFMSC in methanol-water, ethanol-water, and acetone-water at 45 °C are summarized in Table 1. The Table 1 reveals that the rate increases in the order acetone-water < ethanol-water < methanol-water. The constant varies slightly as the water content of the mixtures increases; this means that the rate is slightly affected by the solvent with higher ionizing power,  $Y$ , suggesting that bond breaking in the transition state is of little importance. First-order rate constants for solvolysis of TFMSC vary over only a eight-fold range in alcohol-water mixtures, whereas the observed first-order rate constants for

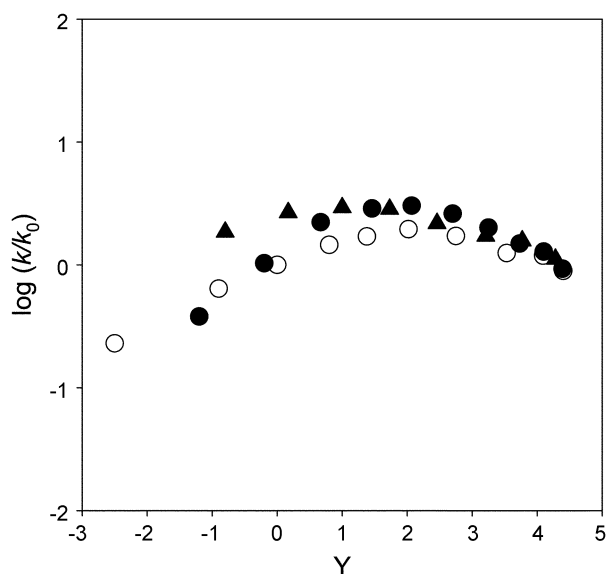
**Table 1.** Rate constants for solvolysis of trifluoromethanesulfonyl chloride in aqueous alcohol and acetone binary solvent mixtures at 45 °C<sup>a</sup>

v/v %	MeOH	EtOH	Acetone
	$k \times 10^4$		
100	0.248	0.150	
90	0.673	0.419	
80	1.45	0.653	1.21
70	1.89	0.950	1.74
60	1.98	1.11	1.91
50	1.70	1.28	1.86
40	1.31	1.12	1.42
30	0.972	0.815	1.12
20	0.837	0.776	1.03
10	0.606	0.596	0.729
H <sub>2</sub> O	0.518	0.518	0.518

<sup>a</sup>Determined conductometrically at least in duplicate; typical error  $\pm$  3%.

benzyl chloride, *p*-methoxybenzoyl chloride and thenoyl chloride which are known to react *via* an  $S_N2$  or  $S_N1$  reaction mechanism varying over several thousand-fold range.<sup>12</sup> These results indicate that the rate determining step is the bond breaking step, which was found in the reaction of  $S_N1$  or  $S_N2$  substrate, but the rate determining step is the addition step for the reaction of addition-elimination ( $S_{AN}$ ) substrate where transition state is not sensitive to the solvent ionizing power. These results are very similar to those of solvolytic reactions of furoyl chloride,<sup>13a</sup> *p*-nitrobenzoyl chloride,<sup>14</sup> *p*-nitrobenzenesulfonyl chloride,<sup>15</sup> and phenyl chloroformates,<sup>6</sup> but they are different from the results of solvolytic reactions of benoyl chloride,<sup>13b</sup> benzyl chloride,<sup>14b</sup> and *p*-methoxybenzoyl chloride.<sup>14c</sup>

The Grunwald-Winstein plots (equation 1) of the rates in Table 1 are presented in Figure 1 using the solvent ionizing

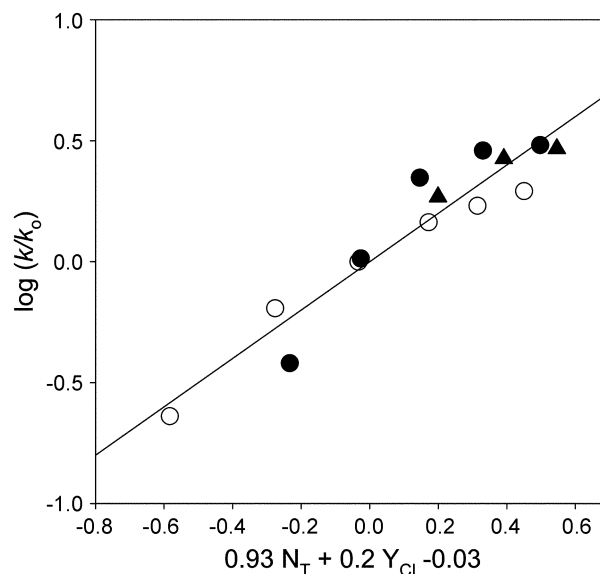
**Figure 1.** Logarithms of first-order rate constants for solvolysis of trifluoromethanesulfonyl chloride at 45 °C  $\log(k/k_0)$  vs.  $Y_{Cl}$  (solvent codes: ●; methanol, ○; ethanol, ▲; acetone).

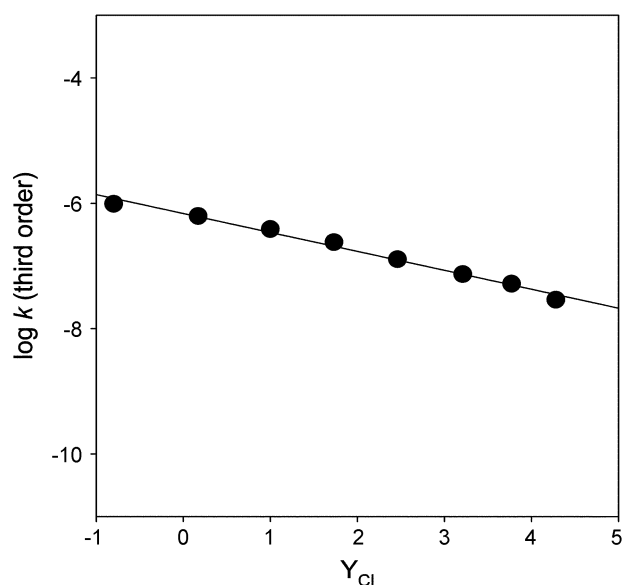
power scale  $Y_{Cl}$ , based on 1-adamantyl chloride.<sup>16</sup> The plots are curved upwardly with three separate lines. The slopes ( $m$ ) for the range of relatively good linearity are very small values of  $m = 0.28$  ( $r = 0.919$ ),  $m = 0.21$  ( $r = 0.971$ ), and  $m = 0.30$  ( $r = 0.922$ ) for the ranges of 100 M-60 M, 100E-50E, and 80A-60A, respectively, implying that the solvolysis of TFMSC in the binary mixtures proceeds by addition-elimination ( $S_{AN}$ ) or associative  $S_N2$  channel.

In order to examine the cause of dispersion phenomenon, we correlated the rate data in table using eqn. (2). The nucleophilicity parameter ( $N_T$ ) have been shown to give a good correlation when an  $lN_T$  term are added to the original Grunwald-Winstein [eqn. (1)] correlations of solvolysis of TFMSC. Therefore such phenomenon can be explained as dispersion effect caused by solvent nucleophilicity parameter. With use of the extended Grunwald-Winstein eqn. (2), the  $l$  and  $m$  values are 0.93 and 0.20 for the solvolysis of TFMSC. The ratio of  $l$  and  $m$  value ( $l/m = 4.1$ ) is very similar to those obtained for solvolysis of *p*-chlorobenzoyl chloride ( $l/m = 3.2$ ),<sup>17</sup> *p*-nitrobenzoyl chloride ( $l/m = 3.3$ ), and phenyl chloroformate ( $l/m = 2.9$ ),<sup>18</sup> where there is independent evidence for a  $S_{AN}/S_N2$  pathway with the addition step being rate determining.<sup>19</sup>

Logarithm of third-order rate constants for solvolysis of TFMSC in acetone-water mixtures ( $\log k_{ww} = \log k_{obs}/[H_2O]^2$ ) versus  $Y_{Cl}$  plots are presented in Figure 2. The slope of Figure 3 shows a very small  $m$  value ( $-0.301$ ), implying that the reaction proceeds through the transition state which is not sensitive to the solvent ionizing power.<sup>14a</sup>

In order to examine the non-linear Grunwald-Winstein plot, it is necessary to take into account the stoichiometric solvation effects based on third order rate constants. For corresponding solvolyses in alcohol-water mixtures, interpretations based on a third order mechanism are more complex, but significant new information is available

**Figure 2.** Plot of  $\log(k/k_0)$  for the solvolysis of trifluoromethanesulfonyl chloride against  $(0.93N_T + 0.20Y_{Cl})$ ;  $r = 0.951$ . (solvent codes: ●; methanol, ○; ethanol, ▲; acetone).



**Figure 3.** Logarithms of third-order rate constants ( $k_{\text{obs}}/[\text{H}_2\text{O}]^2$ ) for hydrolysis of trifluoroethanesulfonyl chloride in acetone/water at 45 °C vs.  $Y_{\text{Cl}}$  ( $r = 0.994$ ).

because two products are formed. Thus there are four possible third order rate constants in the solvolysis reaction: (i)  $k_{\text{aa}}$  for a mechanism in which one molecule of alcohol acts as a nucleophile and second molecule acts as a general base; (ii)  $k_{\text{aw}}$  in which alcohol acts as a nucleophile and water acts as a general base; (iii)  $k_{\text{wa}}$  in which water acts as nucleophile and alcohol acts as general base; (iv)  $k_{\text{ww}}$  in which water acts as both nucleophile and general base.<sup>11</sup> Therefore, observed first-order rate constants in alcohol-water mixtures are given by equation (3).

$$k_{\text{obs}} = k_{\text{aa}}[\text{alcohol}]^2 + (k_{\text{aw}} + k_{\text{wa}})[\text{alcohol}][\text{water}] + k_{\text{ww}}[\text{water}]^2 \quad (3)$$

The  $k_{\text{aa}}$  term can be calculated from observed first order rate constants in pure alcohol ( $k_{\text{aa}} = k_{\text{obs}}/[\text{ROH}]^2$ ); similarly  $k_{\text{ww}}$  can be obtained from the observed first order rate constant in water ( $k_{\text{ww}} = k_{\text{obs}}/[\text{H}_2\text{O}]^2$ ).<sup>11c,11d</sup>

It is impossible to separate  $k_{\text{aw}}$  and  $k_{\text{wa}}$  from  $k_{\text{obs}}$ , but  $(k_{\text{aw}} + k_{\text{wa}})$  term can be calculated from  $k_{\text{obs}} - (k_{\text{ww}}[\text{H}_2\text{O}]^2 + k_{\text{aa}}[\text{ROH}]^2)$ .

The third-order rate constants are summarized in Table 2 for solvolysis of TFMSC in aqueous methanol and ethanol. The Table 2 reveals that the  $k_{\text{ww}}$  terms increase with increasing of water content of the mixtures, but the  $k_{\text{aa}}$  terms decrease. The contributions of third-order terms,  $(k_{\text{wa}} + k_{\text{aw}})$  are larger than  $k_{\text{ww}}$  and  $k_{\text{aa}}$  terms, and show a maximum at near 60M and 50E in aqueous alcohol mixtures. Such an upward curve type rate behaviour was often observed<sup>6a,c,d,14b</sup> in the Grunwald-Winstein plot for solvolysis of alcohol mixtures.

The maximum value of  $(k_{\text{wa}} + k_{\text{aw}})$  for aqueous ethanol is almost twice larger than aqueous methanol; this means that the nucleophilicity of aqueous ethanol solvents is larger than aqueous methanol solvents.

**Table 2.** Separated third order rate constants for trifluoro-methanesulfonyl chloride solvolyses in aqueous methanol (M) and ethanol (E)

Alcohol % (v/v)	$k / 10^{-6} \text{ s}^{-1}$		
	$k_{\text{aa}}$	$(k_{\text{aw}} + k_{\text{wa}})$	$k_{\text{ww}}$
90M	1.98	2.17	0.0494
80M	1.56	4.77	0.197
70M	1.20	7.86	0.445
60M	0.879	<b>9.45</b>	0.790
50M	0.610	<b>10.9</b>	1.24
40M	0.390	9.04	1.78
30M	0.220	5.51	2.42
20M	0.0980	4.50	3.16
10M	0.0240	1.94	4.00
90E	1.19	5.49	0.0494
80E	0.940	13.4	0.197
70E	0.719	<b>17.6</b>	0.445
60E	0.528	<b>18.5</b>	0.790
50E	0.367	15.4	1.24
40E	0.235	11.1	1.78
30E	0.132	7.17	2.42
20E	0.0590	5.15	3.16
10E	0.0150	2.05	4.00

Assuming general base catalyzed reactions for nucleophilic attack on the substrate, the observed rate,  $k_{\text{obs}}$ , can be given for the reactions in acetone-water mixtures as Eqn. (4).<sup>23,24</sup>

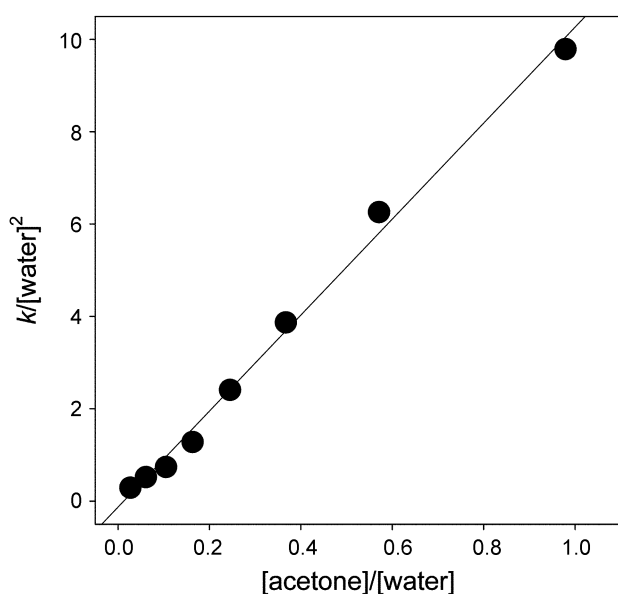
$$k_{\text{obs}} = k_{\text{ww}}[\text{water}]^2 + k_{\text{wa}}[\text{water}][\text{acetone}] + k_{\text{aa}}[\text{acetone}]^2 \quad (4)$$

The third-order rate constant  $k_{\text{wa}}$  can be obtained by the plot of  $k_{\text{obs}}/[\text{water}]^2$  versus  $[\text{acetone}]/[\text{water}]$  (Eqn. 5).

$$k_{\text{obs}}/[\text{water}]^2 = k_{\text{ww}} + k_{\text{wa}}[\text{acetone}]/[\text{water}] \quad (5)$$

This type of plot showed a straight line with a positive slope for the reactions proceeding with an  $S_{\text{N}}2/S_{\text{A}}\text{N}$  mechanism (e.g. solvolysis of *p*-nitrophenyl chloroformate).<sup>6a</sup> And this type of plot showed a leads to an exponential decay curve for the reaction proceeding with an  $S_{\text{N}}1$  mechanism (e.g. solvolysis of cinnamyl halides).<sup>12d</sup> The plot for the solvolysis of TFMSC, leads to a straight line of positive slope, Figure 4. This means that the rate is dependant of the catalysis,  $k_{\text{wa}}$  is existent and independent on the ionizing power of the solvent,  $Y$ . In fact the plot of  $\log k$  (third order) against  $Y_{\text{Cl}}$  (or volume percentage water) shows a straight line with a negative slope (Figure 3). We therefore conclude that the rate is solely dependent on  $k_{\text{wa}}$  (as required for an  $S_{\text{N}}2/S_{\text{A}}\text{N}$  reaction) and the slow step of this reaction is the attack of water molecule and acetone acts as a general base catalysis.

We reported *ab initio* calculations on the hydrolysis and solvolysis of MSC by water methanol, and methanol-water mixtures. In that work, the solvent-catalyzed hydrolysis and methanolysis of MSC with a trigonal bipyramidal transition state in solvent was suggested.<sup>12</sup>



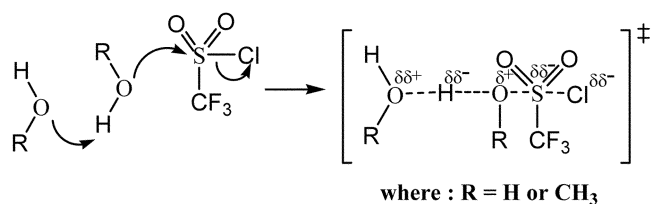
**Figure 4.** Plot of third-order rate constant versus  $[\text{water}]/[\text{acetone}]$  for hydrolysis of trifluoroethanesulfonyl chloride in acetone/water at 45 °C ( $r = 0.997$ ).

These results are in good agreement with the general base catalysis  $S_{\text{AN}}/S_{\text{N}}2^{19}$  reaction mechanism proceeding through a tight transition state, where bond formation is much more progressed than bond breaking in the transition state.

We have plotted the logarithm of rate constants *versus* logarithm of water concentration, which is often referred to as Kivinen plot.<sup>20</sup> The slopes ( $n$ ) of the linear parts were 0.85 ( $r = 0.986$ ) for 100 M-60 M, 0.78 ( $r = 0.997$ ) for 100E-60E. These results are in good agreement with  $S_{\text{AN}}/S_{\text{N}}2^{19}$  reaction mechanism with a tight transition state structure.

The solvent isotope effects for reaction of TFMSC in methanol and water at 45 °C are summarized in Table 4. The solvent isotope effects are relatively large, which suggests that the OH bond at methanol breaks significantly in the transition state.<sup>6c</sup> This is another piece of evidence in support of the  $S_{\text{AN}}/S_{\text{N}}2^{19}$  mechanism in methanol and in water, in which methanol and water molecules act as a general base catalyst, as shown in Scheme 1.

The activation parameters for solvolyses of TFMSC in 50% aqueous ethanol solvents and 50% aqueous methanol solvents at 45 °C are summarized in Table 3. The large negative  $\Delta S^{\ddagger}$  and relatively small positive  $\Delta H^{\ddagger}$  values reveals that the solvolytic reaction proceeds *via* a typical



→ Products  
**Scheme 1**

**Table 3.** Additional rate constants ( $k/s^{-1}$ ) for solvolyses of trifluoromethanesulfonyl chloride in aqueous alcohol mixtures and the activation parameters at 25 °C

	T / °C	$k/s^{-1}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
50% EtOH	25 °C	$0.340 \times 10^{-4}$	11.9	-39
50% EtOH	35 °C	$0.643 \times 10^{-4}$		
30% EtOH	45 °C	$1.28 \times 10^{-4}$		
50% MeOH	25 °C	$0.647 \times 10^{-4}$	8.5	-49
50% MeOH	35 °C	$1.43 \times 10^{-4}$		
50% MeOH	45 °C	$1.70 \times 10^{-4}$		

<sup>a</sup>Calculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg, K. B. *Physical Organic Chemistry*, Wiley: New York, 1964; p 378.) are  $\pm 0.5$  kcalmol<sup>-1</sup> and  $\pm 2$  eu for  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$ , respectively.

**Table 4.** Rate constants and kinetic solvent isotope effect of trifluoromethanesulfonyl chloride in methanol and water at 45 °C

Solvent	$k_{\text{SOHa}}$	$k_{\text{SODa}}$	KSIE
	$k \times 10^5$		
Methanol	2.48	0.804	3.08
Water	5.18	2.31	2.24

<sup>a</sup>Determined conductometrically at least in duplicate; typical error  $\pm 3\%$ .

bimolecular reaction.<sup>20</sup> And the value of activation parameters are again in good agreement with our proposed  $S_{\text{N}}2/S_{\text{AN}}$  reaction channels. The magnitude of  $\Delta S^{\ddagger}$  and  $\Delta H^{\ddagger}$  values, suggesting that bond formation is advanced significantly, while bond breaking is of little advanced in the transition state. The variation of activation parameters in two mixed solvents indicates that bond formation is advanced significantly in the transition state, but bond breaking is negligible at the transition state.

## Experimental Section

TFMSC was commercial grade (Wako Gr-grade > 99%). Merk Gr-grade (< 0.1% H<sub>2</sub>O) acetone, ethanol and methanol were used without further purification. D<sub>2</sub>O and CH<sub>3</sub>OD were from Aldrich (99.9% D). Distilled water was redistilled with Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain specific conductivity of less than  $1.0 \times 10^{-6}$  mhos/cm. Rates were measured conductometrically at least in duplicate as in previous work.<sup>30</sup>

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