KINETIC STUDY OF FORMATION OF BISPHENOL A

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The condensation reaction of phenol with acetone in an acidic medium to produce bisphenol A has been studied with and without the use of promoters. The promoters used were thioglycollic acid, ethyl mercaptan, butyl mercaptan and hexyl mercaptan. The kinetic study of the reaction shows a first order dependence of the reaction rate individually on phenol and on acetone. The mercaptans greatly enhance the reaction rate whereas thioglycollic acid appears to be only a moderate promoter. The rate-controlling step of the reaction has been found to be the formation of the intermediate carbinol, 2-(4-hydroxyphenyl)-propan-2-ol.

Introduction

Various conflicting[1-4] reports on the kinetic investigation of the condensation reaction between phenol and acetone in presence of strong acids yielding bisphenol A drew our attention to the problem. Mercaptans[5] are in general, efficient promoters for this reaction. The present paper is devoted to the study of the reaction kinetics using thioglycollic acid (T.G.A.) and ethyl, butyl and hexyl mercaptans as promoters in the hydrogen chloride catalysed condensation reaction under anhydrous condition.

Experimental

The experiment was conducted in a closed system adequately provided with stirring and reflux arrangements. Desired reactant concentrations were obtained by mixing appropriate volumes of (a) a mixture of phenol and acetone and (b) hydrogen chloride dissolved in acetone. The hydrogen chloride concentration was determined by acidimetry. The course of reaction was followed by estimating (1) acetone by the hydroxylamine hydrochloride[6] method after neutralising the acid originally present in the aliquots and (2) bisphenol A by a spectrophotometric method developed by the authors.[7] The amount of phenol was calculated from that of bisphenol A, based on the stoicheiometry of the reaction and assuming side reactions involving phenol as practically negligible.

Results

Evaluation of the rate constant for the reaction by the integral method applying the 2nd order integral rate equation:

$$K' = \frac{2 \cdot 303}{(p-2a)t} \cdot \log \frac{a(p-2x)}{p(a-x)}$$

for the reaction

2(Phenol) + Acetone → Bisphenol A + Water,
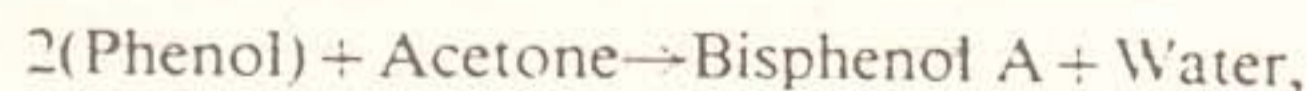
where K' = apparent rate constant, l/mole/sec, t = time in sec, x = concentration of bisphenol A in time t, moles/l, a = initial concentration of acetone, moles/l, and p = initial concentration of phenol, moles/l, gives fairly constant values of K' at fixed concentrations of acid and promoter (when present). For example, $K' = 8 \cdot 28 \times 10^{-6}$ l/mole/sec at 45° when acid concentration was $1 \cdot 0$ moles/l and $K' = 2 \cdot 59 \times 10^{-5}$ l/mole/sec at 45° when acid concentration was $1 \cdot 0$ moles/l and T.G.A. concentration was $0 \cdot 0786$ moles/l which exhibits first order dependence independently on phenol and on acetone. This shows that the trimolecular reaction is kinetically a second order one.

K' is again a composite quantity and found to be:

$$K' = K'_1(H^+) + K'_2(H^+).(\text{Promoter})$$

where K'_1 and K'_2 are constants,

because plots of K' vs. (Promoter) yield good straight lines at different acid concentration with the intercept and slope being linear functions of (H^+). Fig. 1 shows how K' for both promoted and unpromoted reactions varies with (H^+). Thus the rate of expression may be more explicitly written as:

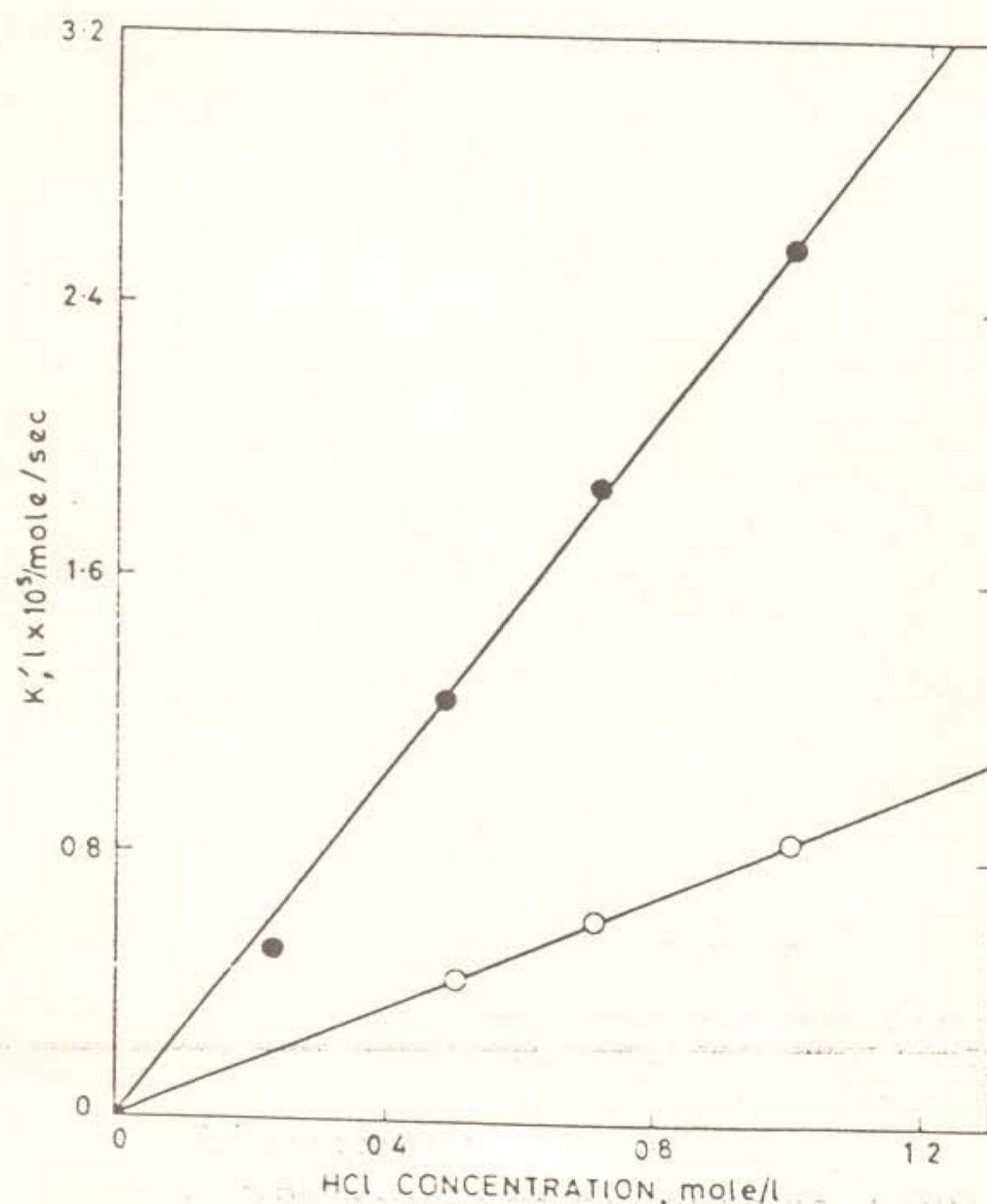Rate of formation of bisphenol A = $[K'_1(H^+) + K'_2(H^+).(\text{Promoter})].(\text{Phenol}).(\text{Acetone})$

Fig. 1. *Variation of apparent rate constant* (K') *with acid concentration*

○————○ without promoter ●————● with promoter
(T.G.A. 0·0786 mole l at 45°)

The activation energy is 11·52 kcal/mole for unpromoted and 10·60, 10·23, 10·23 and 6·8 kcal/mole for thioglycollic acid, hexyl, butyl and ethyl mercaptan promoted reactions respectively.

Further, it was found that the rate is promoted to the same extent by T.G.A. and the thioketals prepared from acetone and T.G.A.[8] or from methyl ethyl ketone and T.G.A.

Discussion

The reaction order tallies with that reported by Vladimer[1] et al. but differs from the results of Tokio Kato[2] who observed the reaction to be of 3rd order, 1st order with respect to acetone and 2nd order with respect to phenol. The kinetic results can best be explained by the following reaction scheme.
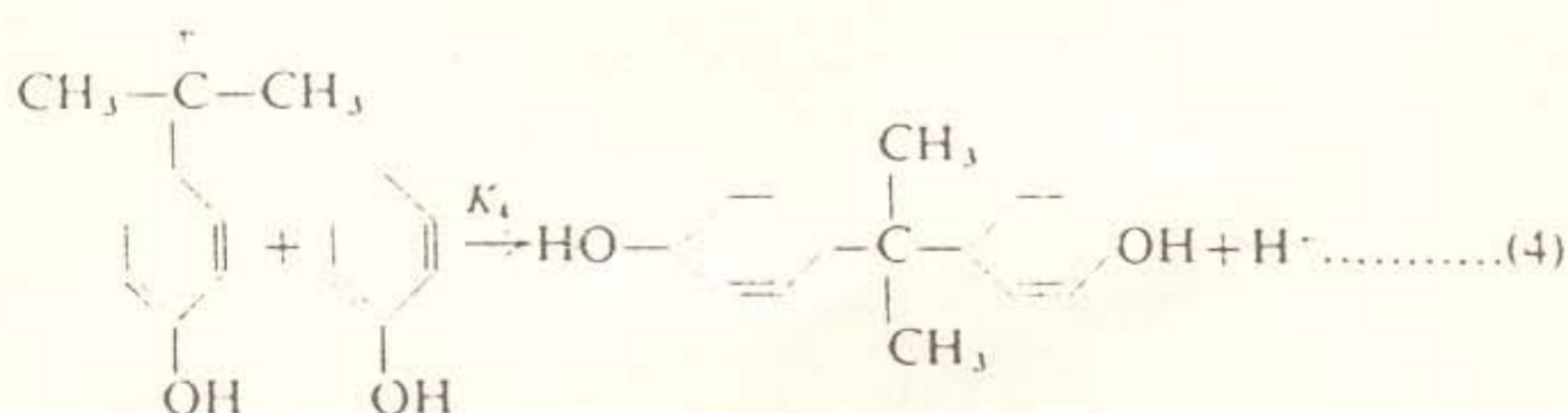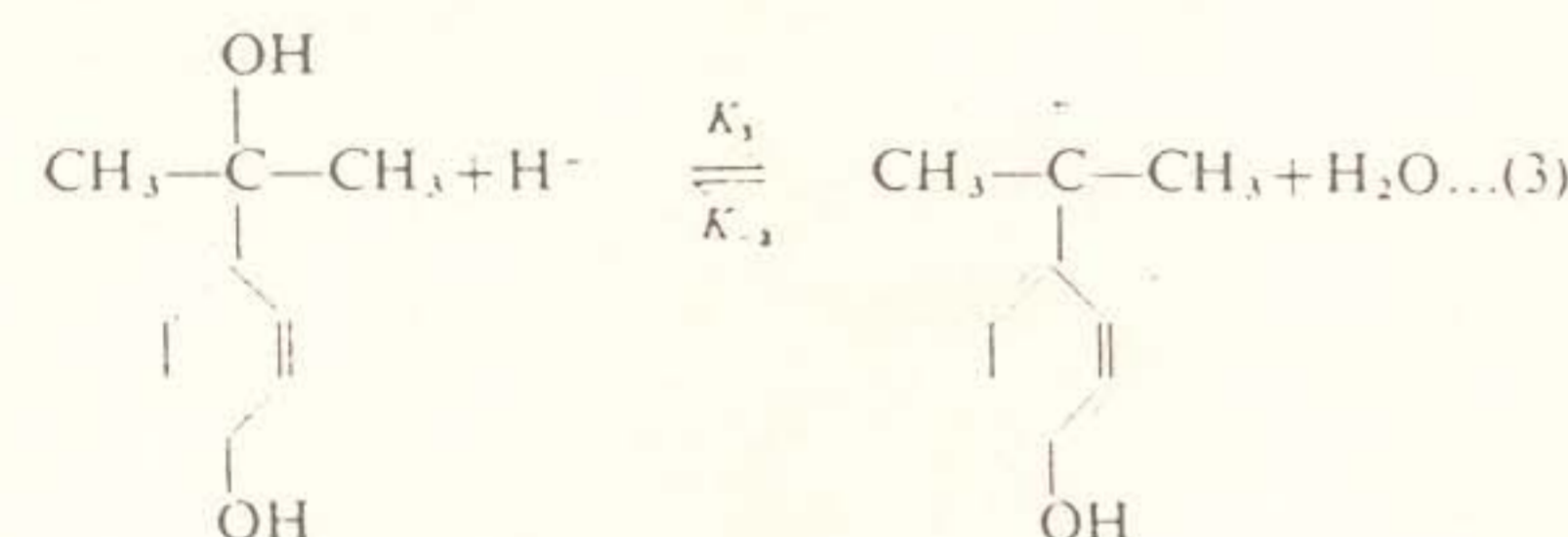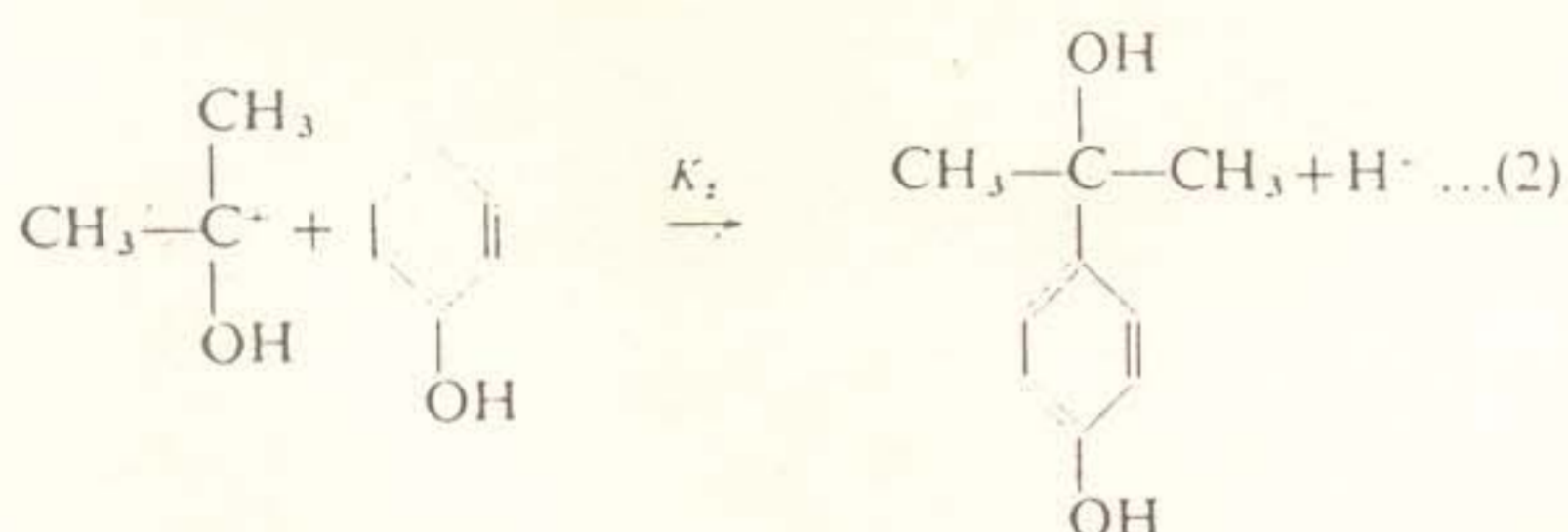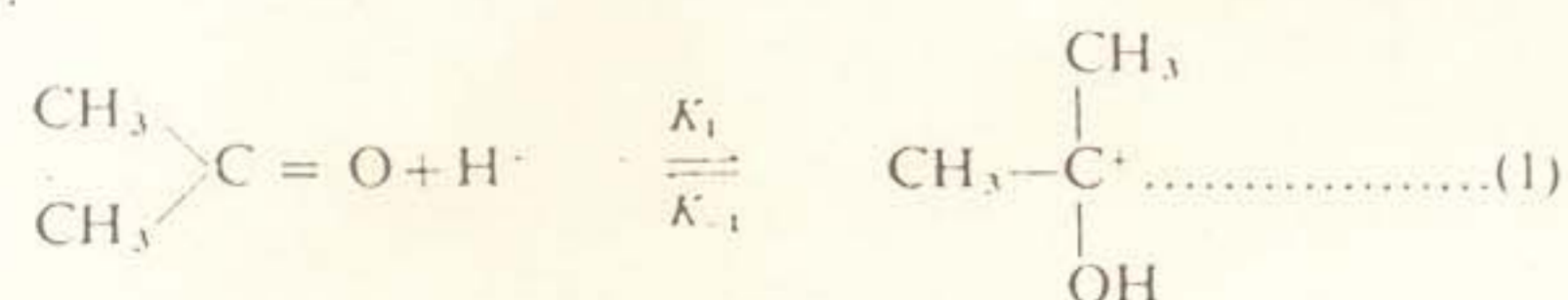
Assumption of step (2) as the rate-determining step and application of stationary state treatment yields:

$$+ \frac{d}{dt}[\text{bisphenol A}] = \frac{K_1 K_2}{K_{-1}}[H^+][\text{acetone}][\text{phenol}]$$

$$= K''(\text{acetone})(\text{phenol})$$

where $K'' = K_1 . K_2 [H^+]/K_{-1}$ and is a constant at fixed $[H^+]$. This agrees well with the experimental results. Braun[3] postulated the intermediate formation of *p*-isopropenyl phenol as the rate-determining step while de Jong & Dethmers[4] postulated the formation of 2-(4-hydroxyphenyl)propan-2-ol from acetone and phenol as the rate-determining step as assumed above.

As to the promoting effect of mercaptans, the increase in K' values is not reflected in the overall activation energy lowering except in case of ethyl mercaptan. Other factors might therefore be operating.

It is quite likely that the mercaptan-promoted reaction proceeds via the intermediate formation of hemithio ketals and thio ketals respectively. In support of this view the much greater reactivity of mercaptols[9] with phenol against that of pure ketones with phenol can be cited.

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