STUDY ON CLEAVAGE OF TETRAMETHYLDIPHENYLDISILANE BY BROMINE

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Recently the investigation of compounds containing silicon — silicon bond and that of the Si—Si bond itself has come more and more into the limelight. Although the readiness of Si—Si bond to be cleavaged has already been examined in various disilanes, quantitative results are hardly available on the rate of these reactions. The Si—Si bond is much more stable in hexaphenyldisilane than the C—C bond in hexaphenylethane [1]. The hexaphenyldisilane can be cleavaged with alkali metals, it does not react with iodine; bromine in carbon tetrachloride solution brings about slow decomposition while forming triphenylbromosilane [2—5]. Hexaalkyldisilanes can easily be cleavaged with bromine and iodine producing the respective alkylhalogenosilane [6]. The results of reaction kinetic investigations on the cleavage of alkyldisilanes with iodine and bromine, published up to the present [7] are compiled in Table 1.

Table 1

Reaction rate constants and activation energy of cleavage of Si—Si bond

Compound	k · 10^{-8} (litre/mol · sec)		Activation energy (kcal/mol)	
	I_2	Br_2	I_2	Br_2
$[CH_3(C_2H_5)_2Si]_2$	4.93	4500	11.7	5.2
$[(CH_3)_3Si]_2$	6.35	—	10.5	—
$[Cl(CH_3)_2Si]_2$	very slow	59	—	11.8
$(CH_3)_3SiSi(CH_3)_2C_3H_7$	6.93	—	7.8	—
$Cl(CH_3)_2SiSi(CH_3)_3$	0.07	970	—	9.2

In the course of our work we set as aim to study the cleavage of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with bromine. The compound was prepared

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by the reaction of dimethylphenylchlorosilane and sodium in a xylene solution (yield: 40%, m.p.: 35 °C). The cleavage of tetramethyldiphenyldisilane with bromine was carried out in carbon tetrachloride solution. The progress of the reaction was traced up by determining the bromine concentration. The instantaneous concentration of bromine was checked by spectrophotometry. The ultraviolet spectrum of tetramethyldiphenyldisilane has an absorption peak at 235.6 nm, shoulders at 207 and 270 nm and the value of extinction coefficient above 300 nm is practically zero. The spectrum of bromine exhibits a high intensity absorption peak at 420 nm. Therefore the determination of the quantity of bromine in the wavelength band of about 420 nm is not disturbed by the occurring tetramethyldiphenyldisilane. Neither is the measurement of bromine concentration influenced by the dimethylphenylbromosilane formed during the reaction, since the ultraviolet spectrum of phenylbromosilane shows absorption peaks at 218 and 273 nm. The bromine concentration of samples out of the reaction mixture was determined on the basis of spectrophotometric measurements at three different wavelengths (410, 420 and 430 nm) by means of a calibration diagram. The measured data of one experiment are compiled in Table 2. The initial bromine and the initial disilane concentrations are denoted by c_{A_0} and c_{B_0}, respectively.

Table 2

Determination of bromine concentration in the course of experiment 1 (Temperature: 16 °C, $c_{A_0} = 4.08 \cdot 10^{-3}$ mol/litre, $c_{B_0} = 4.08 \cdot 10^{-3}$ mol/litre)

Time (minute)	Extinction	Bromine concentration $\times 10^3$ (mol/litre)
4	0.685	3.38
8	0.590	2.90
12	0.503	2.48
16	0.453	2.23
20	0.404	2.00
24	0.370	1.82
28	0.335	1.65
32	0.310	1.52
36	0.274	1.36
44	0.241	1.19
52	0.208	1.03
60	0.192	0.95
68	0.165	0.82
76	0.150	0.75

The initial concentrations of bromine and disilane and the temperature of the reactions applied in the reactions carried out for investigating the cleavage of tetramethyldiphenyldisilane by bromine are shown in Table 3. c_{A_0} and c_{B_0} values in the table indicate in every case the initial bromine and initial disilane concentrations, respectively. In the course of experiments 1 through 8 the disilane was reacted with bromine of equimolecular quantity at gradually increasing temperatures. The bromine concentration—time diagrams plotted from measured data are shown in Figs 1 to 3, demonstrating the increase of reaction rate with increasing temperature. In the course of experiments 9 through 15 the reactions were carried out with different bromine–disilane ratios to determine the order of reaction and the partial order of the components in the reaction. In experiments 16 through 19 the bromine was taken in an excess quantity of 10% referred to the disilane (Figs 4 and 5).

Table 3

Initial concentration of bromine (c_{A0}) and disilane (c_{B0}) and temperature of the reactions

Number of experiment	c_{A_0} (mol/litre)	c_{B_0} (mol/litre)	Temperature) (°C)
1	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	16
2	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	20
3	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	25
4	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	30
5	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	35
6	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	40
7	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	45
8	$4.08 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$	50
9	$1.904 \cdot 10^{-3}$	$1.904 \cdot 10^{-3}$	25
10	$8.16 \cdot 10^{-3}$	$8.16 \cdot 10^{-3}$	25
11	$3.808 \cdot 10^{-3}$	$3.808 \cdot 10^{-3}$	25
12	$7.616 \cdot 10^{-3}$	$3.808 \cdot 10^{-3}$	25
13	$1.904 \cdot 10^{-3}$	$3.808 \cdot 10^{-3}$	25
14	$3.808 \cdot 10^{-3}$	$1.904 \cdot 10^{-3}$	25
15	$3.808 \cdot 10^{-3}$	$7.616 \cdot 10^{-3}$	25
16	$4.19 \cdot 10^{-3}$	$3.808 \cdot 10^{-3}$	25
17	$2.095 \cdot 10^{-3}$	$1.904 \cdot 10^{-3}$	25
18	$8.38 \cdot 10^{-3}$	$7.616 \cdot 10^{-3}$	25
19	$4.19 \cdot 10^{-3}$	$3.808 \cdot 10^{-3}$	25

To determine the gross reaction order, two methods were used:

(i) Fig. 6 represents the concentration—time diagram of experiments 3, 9 and 10. In a given experiment the initial concentrations of bromine and disilane were identical, but this concentration decreased from test to test as

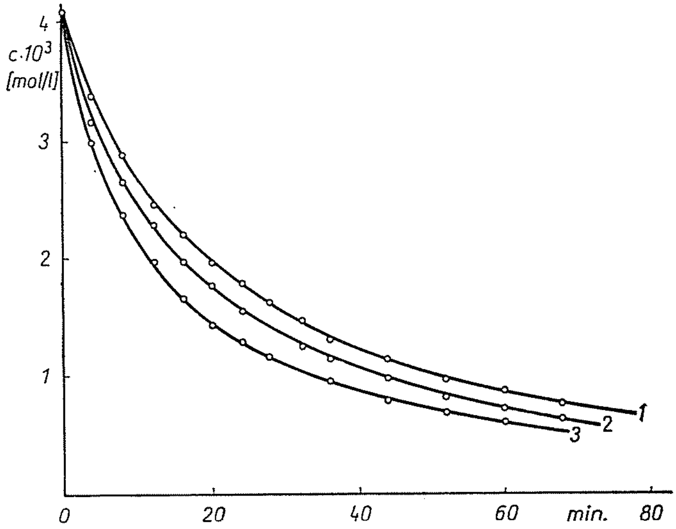

Fig. 1. Concentration—time diagrams of experiments 1—3

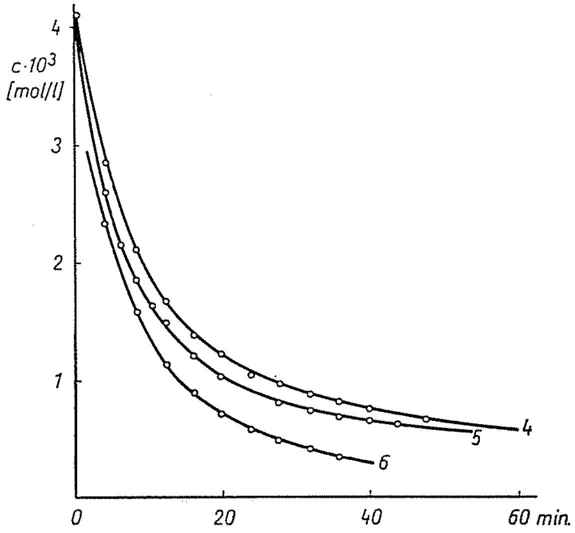

Fig. 2. Concentration—time diagram of experiments 4—6

$c_9 > c_3 > c_{10}$. For each curve the initial slope has been determined which at the same time provided the initial reaction rates (w):

$$w_9 = 6.36 \cdot 10^{-5} \text{ mol/litre} \cdot \text{minute}$$

$$w_3 = 2.72 \cdot 10^{-4} \text{ mol/litre} \cdot \text{minute}$$

$$w_{10} = 1.09 \cdot 10^{-3} \text{ mol/litre} \cdot \text{minute}$$

The reaction order is given by the slope of the $\lg w - \lg c_0$ diagram. Fig. 7 shows points corresponding to the three experiments to lie on an approximately straight line with a slope of 2.007. Thus the reaction order is 2.

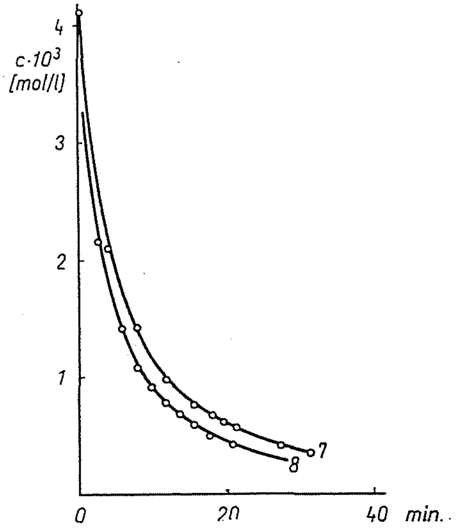

Fig. 3. Concentration—time diagram of experiments 7—8

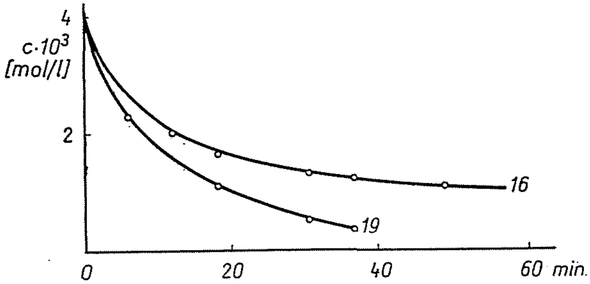

Fig. 4. Concentration—time diagram of experiments 16 and 19

(ii) The reaction order can be determined from data of a single experiment, plotting reaction rates at different times vs. bromine concentration to log-log scale.

The slope of the straight line gives again the gross reaction order.

Calculations were carried out for experiments at different temperatures and different initial concentrations. The lg $\Delta c/\Delta\tau$—lg Δc functions plotted

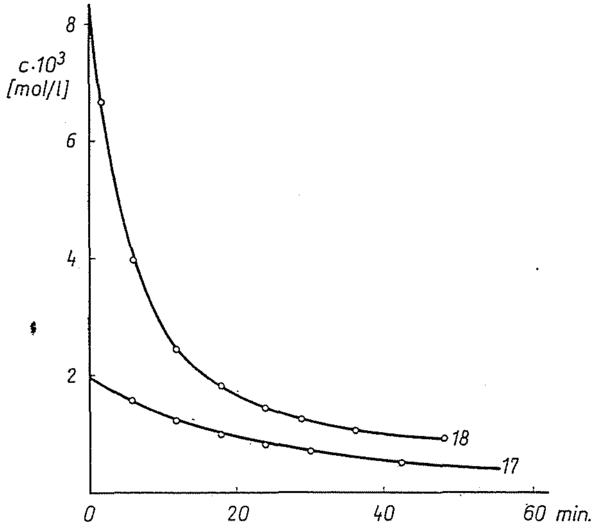

Fig. 5. Concentration—time diagram of experiments 17 and 18

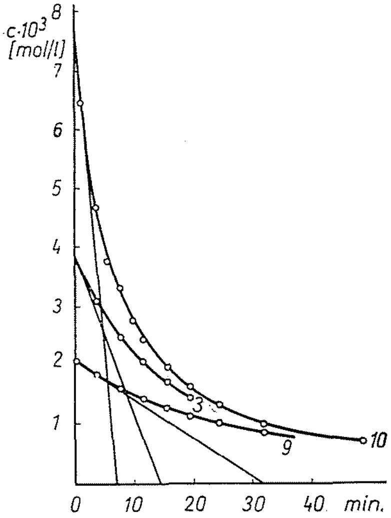

Fig. 6. Concentration—time diagram of experiments 3, 9 and 10

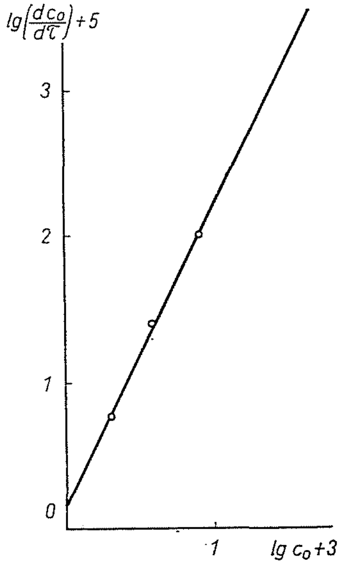

Fig. 7. Determination of reaction order from the initial reaction rates

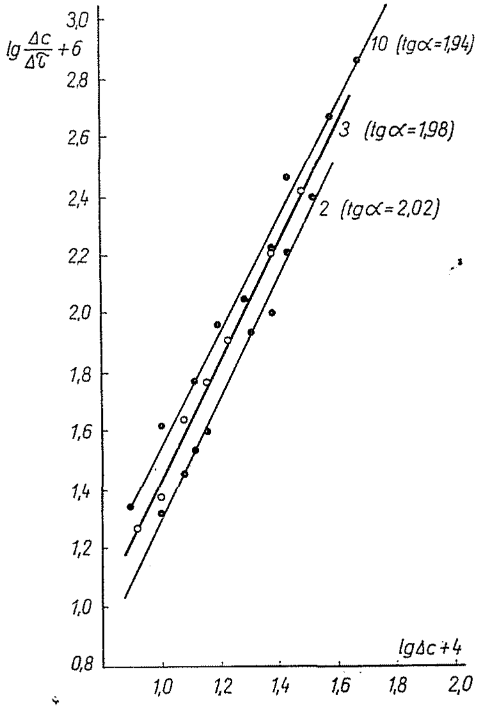

Fig. 8. Determination of reaction order on the basis of experiments 2, 3 and 10

from data of experiments 2, 3 and 10 are represented in Fig. 8. Slope of straight lines of the kind plotted from data of the other experiments prove unambiguously that the reaction between tetramethyldiphenyldisilane and bromine is of second order.

Also the partial reaction orders related to each component have been determined. Experiments 11, 12 and 13 established the partial order of bromine identical with initial concentrations of disilane ($3.808 \cdot 10^{-3}$ mol/litre), while the initial bromine concentrations were chosen to be different:

$$c_{13} = 1.904 \cdot 10^{-3} \text{ mol/litre}$$

$$c_{11} = 3.808 \cdot 10^{-3} \text{ mol/litre}$$

$$c_{12} = 7.616 \cdot 10^{-3} \text{ mol/litre}$$

The initial bromine concentrations are related as:

$$c_{13} : c_{11} : c_{12} = 1 : 2 : 4$$

The bromine concentration—time diagrams related to these three reactions are presented in Fig. 9. The initial slopes of each curve provide the initial reaction rates:

$$w_{13} = 1.21 \cdot 10^{-4} \text{ mol/litre} \cdot \text{minute}$$

$$w_{11} = 2.46 \cdot 10^{-4} \text{ mol/litre} \cdot \text{minute}$$

$$w_{12} = 4.75 \cdot 10^{-4} \text{ mol/litre} \cdot \text{minute}$$

The three reaction rates are related as:

$$w_{13} : w_{11} : w_{12} = 1 : 2.03 : 3.93$$

The ratio of the initial rates practically agrees with that of the starting bromine concentrations, accordingly the partial order of bromine in the reaction is 1.

The partial order related to disilane can be determined in a similar way. In experiments 11, 14 and 15 (Fig. 10) the initial bromine concentration was the same and the disilane concentration changed in every experiment:

$$c_{14} = 1.904 \cdot 10^{-3} \text{ mol/litre}$$
$$c_{11} = 3.808 \cdot 10^{-3} \text{ mol/litre}$$
$$c_{15} = 7.616 \cdot 10^{-3} \text{ mol/litre}$$

The initial concentrations of disilane are related as:

$$c_{14} : c_{11} : c_{15} = 1 : 2 : 4$$

The starting reaction rates can be calculated on the basis of the initial slopes:

$$w_{14} = 1.31 \cdot 10^{-4} \text{ mol/litre} \cdot \text{minute}$$
$$w_{11} = 2.55 \cdot 10^{-4} \text{ mol/litre} \cdot \text{minute}$$
$$w_{15} = 5.42 \cdot 10^{-4} \text{ mol/litre} \cdot \text{minute}$$

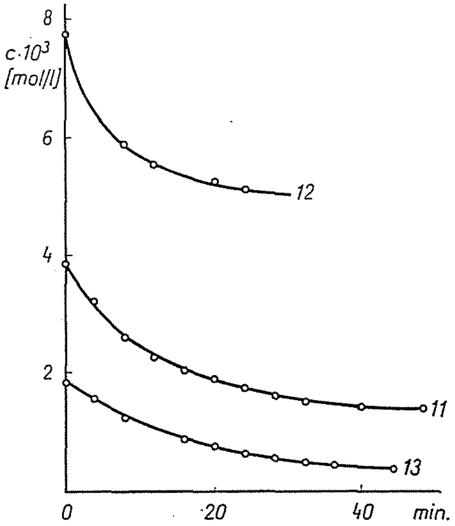

Fig. 9. Concentration—time diagram of experiments 11—13

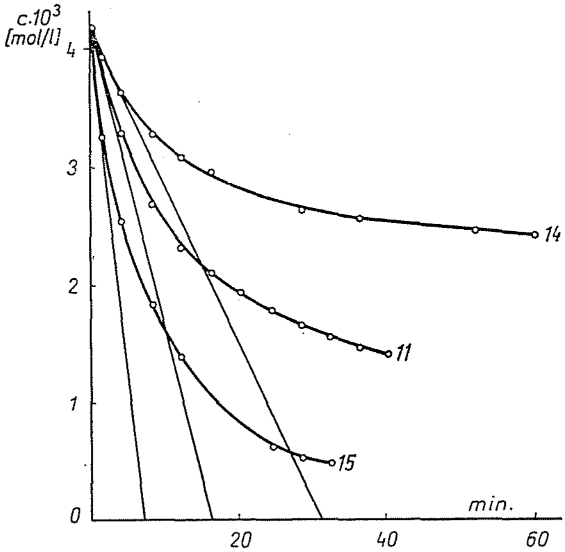

Fig. 10. **Determination of partial reaction order of tetramethyldiphenyldisilane on the basis of reaction 11, 14 and 15**

The three reaction rates are related as:

$$w_{14} : w_{11} : w_{15} = 1 : 1.95 : 4.14$$

Also in this case, the ratio of the initial rates practically agrees with that of the initial disilane concentrations, the partial order of disilane in the reaction is 1.

Because of the second order of reaction the cleavage is likely to occur by ionic mechanism. In the course of bromine attack an intermediate complex is formed in which silicone is in hybrid state sp^3d; in addition bromide ion yields. After this the Si—Si bond splits producing dimethylphenylbromosilane and dimethylphenylsilyl cation. The reaction is finished by the attachment of the dimethylphenylsilyl cation and the bromide ion.

In measurements 16 through 19 a 10 per cent excess of bromine was used. Comparison of these reaction rates with those of equimolecular initial concentration, under otherwise identical conditions (of temperature and disilane concentration) shows that an increase of bromine concentration results in a higher reaction rate.

In the case of identical concentrations of bromine and disilane where the reaction is of second order, the rate constant k can be calculated at any time from the equation:

$$k = \frac{1}{\tau}\left(\frac{1}{c_A} - \frac{1}{c_{A_0}}\right),$$

where τ is the time, c_A is the concentration at time τ, c_{A_0} is the initial concentration. The rate constant value is practically constant throughout one reaction.

The change of the mean value of the rate constant as a function of reaction temperature is compiled in Table 4.

Table 4

Value of rate constant at different temperatures

Temperature (°C)	k (litre/mol · minute)
16	12.56
20	15.53
25	21.00
30	27.85
35	34.33
40	56.01
45	63.26
50	86.48

Fig. 11 represents the relation between the logarithm of the rate constant and the reciprocal value of temperature expressed in Kelvin degrees. The points lie on an approximately straight line. The slope of the straight line was calculated by the least squares method:

$$\mathrm{tg}\,\alpha = 2.3 \cdot 10^{-3}$$

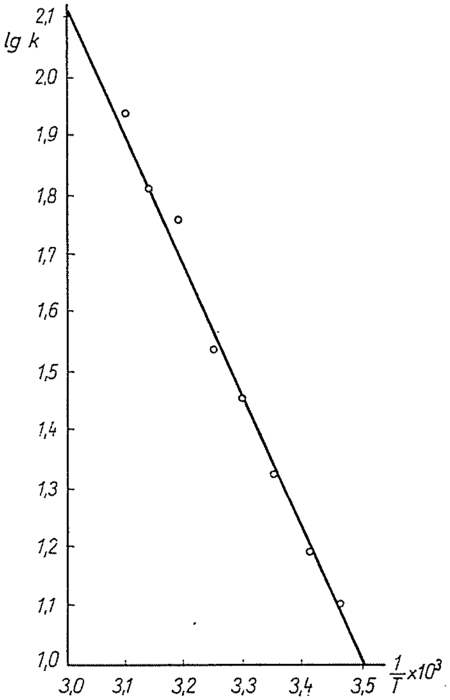

Fig. 11. Dependence of rate constant upon temperature

The activation energy $\Delta H^{\ddagger}$ of the reaction is given by the equation:

$$\mathrm{tg}\,\alpha = -\frac{1}{2.303} \cdot \frac{\Delta H^{\ddagger}}{R}$$

Its value is 10.52 kcal/mol. The dependence of the rate constant upon the temperature is expressed by the equation:

$$k = A \cdot \mathrm{e}^{-\Delta H^{\ddagger}/RT}$$

giving the value of A action constant, i.e. $1.05 \cdot 10^{9}$ litre/mol · minute. The activation entropy $\Delta S^{\ddagger}$ of the reaction at 25 °C is determined by the equation:

$$A = k_t \cdot \frac{298\,k_B}{h} e^{\Delta S^{\ddagger}/R}$$

where the value of transmission coefficient k_t is approximately 1, the universal frequency factor k_B/h is $1.2505 \cdot 10^{12}$ degree^{-1} · minute^{-1}. Thus the activation entropy $\Delta S^{\ddagger} = -25.40$ cal/mol · degree.

Summary

The cleavage of Si—Si bond in tetramethyldiphenyldisilane by bromine has been investigated. The progress of the reaction has been followed by means of ultraviolet spectrophotometry. The order of the reaction, the activation energy and activation entropy of the reaction have been determined.

References

1. Wu, T. C.—Gilman, H.: J. Org. Chem. **23**, 913 (1958).
2. Gilman, H.—Wu, T. C.: J. Am Chem. Soc. **73**, 4031 (1951).
3. Gilman, H.—Wu, T. C.: J. Org. Chem. **18**, 753 (1953).
4. Brook, A. G.—Gilman, H.: J. Am. Chem. Soc. **76**, 287 (1954).
6. Gilman, H.—Ingham, R. K.—Smith, A. G.: J. Org. Chem. **18**, 1743 (1953).
7. Taketa, A.—Kumada, M.—Tarama, K.: J. Chem. Soc. Japan, Pure Chem. Sect. **78**, 999 (1957).

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