$$\underset{CH_3}{\overset{CH_3}{\diagdown}}Si\underset{Cl}{\overset{Cl}{\diagup}} + 2K(Na) \longrightarrow \underset{CH_3}{\overset{CH_3}{\diagdown}}Si: + 2KCl$$
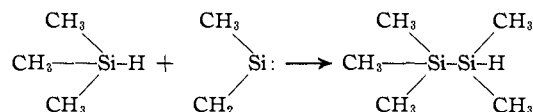
if trimethylsilane, $(CH_3)_3SiH$, is added to the helium stream the dimethylsilene inserts into the Si–H bond to produce pentamethyldisilane.[2,3]

$$CH_3\text{—}\underset{CH_3}{\overset{CH_3}{|}}Si\text{–}H + \underset{CH_2}{\overset{CH_3}{\diagdown}}Si: \longrightarrow CH_3\text{—}\underset{CH_3}{\overset{CH_3}{|}}Si\text{-}\underset{CH_3}{\overset{CH_3}{|}}Si\text{–}H$$

Dimethylsilene was generated from dimethyldichlorosilane (5.9 g.) in the presence of a 10-fold excess of trimethylsilane. The excess trimethylsilane was separated by low temperature distillation and the higher boiling materials by gas chromatography to yield 1.8 g. of pure pentamethyldisilane (30% of theoretical).

The pentamethyldisilane was identified by infrared, proton magnetic resonance, and mass spectra which proved it to be identical with an authentic sample.

Earlier reports claiming dimethylsilene intermediates in condensed systems are considered to be ambiguous.[4,5] To the best of our knowledge no previous experimental chemical observations require a bivalent silicon intermediate.[6]

There do not seem to be satisfactory alternative hypotheses to explain the formation of pentamethyldisilane. A radical chain process involving $(CH_3)_2$-$SiCl$ and $(CH_3)_3Si$ radicals can be eliminated since trimethylsilyl radical generated under comparable conditions couples in good yield to hexamethyldisilane. For example, from either trimethylchlorosilane alone or a mixture of methylene bromide and trimethylsilane, reaction with alkali metal vapor produces hexamethyldisilane. From the reaction of dimethyldichlorosilane-trimethylsilane mixtures, at most a trace of hexamethyldisilane could be detected among the products.

These observations not only implicate a dimethylsilene intermediate, but also suggest it is in the singlet state. Spin conservation rules require that a triplet dimethylsilene react with trimethylsilane to produce two monoradicals for which geminate coupling is precluded. Nongeminate coupling should lead to hexamethyldisilane, pentamethyldisilane, and sym-tetramethyldisilane in 1:2:1 ratios. The homo-

$$(CH_3)_2Si\uparrow\uparrow + (CH_3)_3SiH \longrightarrow (CH_3)_2\dot{S}iH\uparrow + (CH_3)_3\dot{S}i\uparrow$$
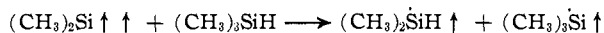
coupling products could not be identified, and all products other than pentamethyldisilane in the ap-

(2) D. Seyferth and J. Burlitch, J. Am. Chem. Soc., 85, 2667 (1963).

(3) K. Kramer and A. Wright, Angew. Chem., 74, 468 (1962); Tetrahedron Letters, 1095 (1962).

(4) F. Johnson and R. S. Gohlke, ibid., 1291 (1962), and private conversation with Dr. Johnson.

(5) R. West and R. E. Bailey, J. Am. Chem. Soc., 85, 2871 (1963).

(6) The work reported in ref. 3 and 4 raised doubts about the necessity of postulating a dimethylsilene intermediate in condensed phase reactions of polysilanes, [(CH₃)₂Si]ₓ, or (CH₃)₂SiCl₂ + Na, with tolane [M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, Tetrahedron, 18, 107 (1962)]. In private communication, however, Dr. Volpin suggests that the best explanation of their results is essentially as proposed in the 1962 publication, adding to the rationalization a final step in which the silacyclopropene (or the diradical derived from it) undergoes dimerization to a 1,4-disilacyclohexadiene. Analogous rationalizations are made in publications by O. M. Nefedow and co-workers [Angew. Chem., in press; Bull. Acad. Sci. USSR Div. Chem. Sci., 1152 (1962)] describing liquid phase reactions of alkali metals with dichlorosilanes and olefins. See also H. Gilman, Angew. Chem., 74, 950 (1962).

propriate molecular weight range summed to 4% of the pentamethyldisilane. For this reason dimethylsilene is assigned a singlet state electronic configuration. For kinetic reasons which will be developed elsewhere this is also considered to be the ground state.

The carbon analogs of dimethylsilene, alkylcarbenes, are not generally trapped in bimolecular processes, but instead rearrange to olefinic products.[7] This

$$(CH_3)_2C: \longrightarrow CH_3\text{—}CH\text{=}CH_2$$

pathway is not favored for dimethylsilene because of the relative instability of the silicon to carbon double bond (no example reported to date). This inability of $(CH_3)_2Si$: to stabilize itself by the above internal rearrangement should increase the probability of bimolecular processes such as insertion into the C–H bonds. However, insertions into the C–H bonds of ethane and trimethylsilane are of low efficiency. These facts suggest that dimethylsilane is much less reactive than singlet CH_2.

(7) R. A. Holroyd and F. E. Blacet, J. Am. Chem. Soc., 79, 4830 (1957).

DEPARTMENT OF CHEMISTRY   P. S. SKELL
THE PENNSYLVANIA STATE UNIVERSITY   E. J. GOLDSTEIN
UNIVERSITY PARK, PENNSYLVANIA

Number of Particles in Colloidal Suspensions of Silver Bromide

Sir:

In an investigation of the particle size and stability of colloidal aqueous suspensions of silver bromide, suspensions were formed at widely different concentrations of reactants and in the presence of ethanol or of acetone and of complexing agents for silver(I). This communication describes the remarkably simple relation that exists under certain conditions between the number of colloidal particles in suspensions of different ages and the initial supersaturation of the suspension. Light scattering methods[1] were used for measurement of particle diameter from about 2 min. up to several days after mixing the reactants. Since the formation of silver bromide is complete (shown by electrical conductivity) within less than 2 min. after mixing,[2] the concentration of suspended material is known and the number of particles, assumed spherical, can be calculated from the diameter. Deviations from spherical shape and from monodispersity exist[2] but are of minor consequence for the present purpose.

Figure 1 is a plot of $\log n$ vs. $\log \sigma$ where n is the number of particles per ml. of suspension, and σ is the initial supersaturation, equal to the concentration of silver bromide at the instant of mixing divided by the solubility at equilibrium. The sols illustrated in Fig. 1 were prepared by addition over about 30 sec. of a solution of silver nitrate to an equal volume of potassium bromide, the latter being stirred at 900 r.p.m. Other details were similar to those reported before.[2] The concentrations of sol and of bromide, which was always in excess over silver, ranged from 5×10^{-3} to 5×10^{-7} M. Under these conditions dissolved

(1) E. J. Meehan and W. H. Beattie, J. Phys. Chem., 64, 1006 (1960).

(2) E. J. Meehan and W. H. Beattie, ibid., 65, 1522 (1961).

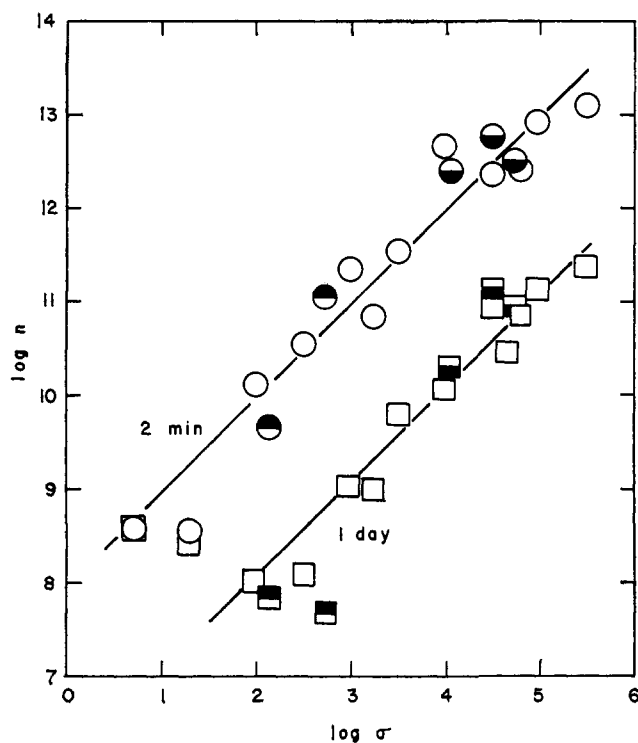Fig. 1.—Log n vs. log σ; silver nitrate added to silver bromide, circles or squares, 2 min. or 1 day, respectively, after mixing; ◑, ◨ in 10, 50, or 90 vol. % ethanol; ◐, ◨ in 50 vol. % acetone. Lines have unit slope.

silver was present as Ag^+, $AgBr(aq)$, or $AgBr_2^-$. The following equilibrium data were used to calculate the solubilities: $(Ag^+)(Br^-) = 5 \times 10^{-13}$; $(AgBr(aq)) = 1 \times 10^{-8}$; $(AgBr_2^-) = 1 \times 10^{-5}(Br^-)$. Ethanol (10, 50, or 90 vol. %) or acetone (50 vol. %), when present, was added both to the silver nitrate and potassium bromide solutions. The solubilities in these solvents were estimated from the work of Krahtovil and Tezak.[3] The equilibrium constant for formation of $AgBr_2^-$ increases with increasing content of ethanol or acetone, and the solubility at moderate $(10^{-3}-10^{-4}\ M)$ concentrations of bromide is larger than in the absence of ethanol or acetone, although the solubility product is much smaller than in water. The lowest calculated values of σ in the mixed solvents are uncertain because no data appear to be available for the concentration of undissociated silver bromide.

Figure 1 shows that at 2 min. after formation, n is remarkably close to proportional to σ. The relation, $\log n = 8.0 + \log \sigma$, applies over nearly five orders of magnitude and includes both aqueous and aqueous organic suspensions. As the sols age and the particles grow (with the exceptions mentioned below) the values of n decrease but n remains proportional to σ. This is illustrated in Fig. 1 by the data for 1 day after mixing, by which time the diameter in most sols is close to the final diameter.[2] At 1 day, $\log n = 6.1 + \log \sigma$; hence the values of n decrease about 80-fold from the values at 2 min. One-day old sols prepared at the lowest values of σ deviate from the linear relation, because in such sols there is practically no particle growth after 2 min. (compare circles and squares, Fig. 1, at $\log \sigma = 0.7$ and 1.3). Reversal of the order of addition (excess of bromide added to silver)

(3) J. Krahtovil and B. Tezak, *Arhiv kem.*, **26**, 243 (1954).

causes an increase in particle size, and hence a decrease in n, at 2 min.; however, at 1 day after mixing the relation between n and σ is the same as shown in Fig. 1. Sols prepared in the presence of ammonia or ethylenediamine tetraacetate generally deviate from the linear relations of Fig. 1, apparently because the initial growth pattern is changed drastically.

CHEMISTRY DEPARTMENT   E. J. MEEHAN
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA 55455

CHEMISTRY DEPARTMENT   GRACE CHIU
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

Photochemical Addition of Benzo[a]pyrene to Pyrimidine Derivatives[1]

Sir:

We have found that the carcinogenic hydrocarbon benzo[a]pyrene (I) forms stable addition products with uracil, thymine, cytosine, 5-methylcytosine, guanine, and 6-azathymine upon irradiation with ultraviolet light.[2] The reaction proceeds even when wave lengths below 320 mμ are filtered out. Since the pyrimidine derivatives do not absorb above 320 mμ, the hydrocarbon is the primary chromophore. Pyrimidine, 2-aminopyrimidine, purine, adenine, dihydrouracil, and dihydrothymine do not react; thus, the presence of a conjugated carbonyl group within the pyrimidine ring system is required in order that the reaction may occur.

The reaction is carried out in 4% aqueous sodium dodecyl sulfate (SDS) solution (pH 6–7) containing 0.0001 M hydrocarbon and 0.032 M pyrimidine, in quartz cuvettes or (for large volumes) a continuous-flow irradiation device. During irradiation, the characteristic ultraviolet absorption peaks of the benzpyrene α-band at 404 mμ and p-band at 388, 367, 350, and 333 mμ disappear, and new peaks corresponding to those of the benzpyrene spectrum gradually appear at longer wave lengths. The exact positions of the new peaks depend to some extent on the pyrimidine derivative used (Table I). The reaction mixture itself turns orange due to photooxidation of the benzpyrene. Yields under these conditions vary from 2% or less for uracil to 50% for 5-methylcytosine. Yields improve and may exceed 95% if the reaction is carried out in 0.2 M NaOH.

TABLE I

PRINCIPAL ULTRAVIOLET ABSORPTION MAXIMA OF BENZPYRENE AND ITS PHOTOPRODUCTS IN 4% SDS SOLUTION

	λ_{max}, mμ			
Benzpyrene	404	388	367	350
Photoproduct with				
Uracil	406	397	376	357
Thymine	406	397	377	358
Cytosine	406	397	376	357
5-Methylcytosine	406	397	377	358
6-Azathymine	406	395	375	357
Guanine	409	397	376	357

The reaction product can be isolated by lyophilizing large volumes of the reaction mixture, dissolving the residue in hot 95% ethanol, crystallizing out as much