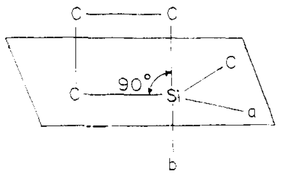
For reactions of R_3SiH with OH^- in 95% ethanol at 35° relative rates (k_2) are, for $(C_2H_5)_3SiH = 1$; I, 10^3; II, 10^4–10^5; $(CH_2)_4Si(CH_3)H$, 10; $(CH_2)_5Si(CH_3)H$, 10^{-1}. For $(C_2H_5)_3SiH$ at 35°, $k_2 = 0.1$ min.$^{-1}$, mole^{-1} l.[5,6]

The corresponding disiloxane, bis-(1-silabicyclo-[2.2.1]heptyl) oxide,[3] m.p. 76°, was isolated in 40% yield (62 mg.) from the kinetics runs with I and perfectly linear pseudo first order plots were obtained. The 4-ring silane, II, gives 60% of the theoretical hydrogen at an extremely fast rate and 40% at a different rate which is smaller than the first by a factor of about three powers of ten. The latter rate has been shown to comprise hydrogen evolution from *sym*-di-*n*-propyldimethyldisiloxane which is formed by ring-opening of II (C-Si cleavage by OH^-) in competition with the evolution of hydrogen from the 4-ring silane.[7]

Thus, it is clear that displacement of hydride ion by hydroxide ion proceeds *far more rapidly* at bridgehead[8] and 4-ring silicon atoms than at silicon in ordinary a-cyclic and 5- as well as 6-ring silicon hydrides. These results comprise a complete reversal of the structure-reactivity relationships observed for displacements at carbon when the same comparisons are made.[9]

The above facts are in accord with the hypothesis outlined in our earlier communication.[3] Thus, in the reaction of II with hydroxide the geometry of the Si(5) addition compound would approximate one of two (idealized) structures: (1) a = H, b = OH; (2) a = OH, b = H.



On the above model of Si(5) complex for II with hydroxide ion[10] and similar models for I and other cyclic and acyclic hydrides, structure-reactivity relations resulting from steric factors are readily explained in terms of three factors: (1) ease of formation of Si(5) resulting from groups on silicon being "pulled back" in Si(4), away from the path of reagent attack. (2) I-Strain in Si(5) relative to Si(4).[11] (3) Steric strain in Si(5) relative to Si(4) due to increased "crowding" of groups in the former.[12]

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[5] Relative rates for the 5- and 6-ring silanes are based on data in R. West, THIS JOURNAL, **76**, 6015 (1954).

[6] Salt effects on k_2 resulting from change in KOH concentration should not appreciably affect the above relative rates tabulation which covers the range 0.003 *N* to 0.2 *N* KOH; see J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 813 (1955).

[7] In 95% ethanol at 35° the 4-ring silane gives 60% of the theoretical hydrogen with an ammonia–ammonium iodide buffer (0.5 *N* NH_3, 0.05 *N* NH_4I) at a rate which corresponds to a half-life of 7.5 minutes. The same reagent gives *no hydrogen* in a reasonable time with the highly reactive triphenylsilane.

[8] Energies of activation, E_a, for $(C_2H_5)_3SiH$ and I are 16 kcal./mole and 7 kcal./mole, respectively. The latter value was calculated from rate data at 0 and −24° using 0.0579 *N* KOH. Relative rate for I at 35° is a calculated value based on the E_a.

[9] For a recent excellent summary of data on effects of ring size on reactivity, see A. Streitwieser, Jr., *Chem. Rev.*, **56**, 666–670 (1956).

[10] There are, of course, four possible structures of Si(5) for II which would have the H-Si-OH angle near 90°, but two of these would be energetically unfavorable since the C-Si-C angle would be constrained from an ideal angle of 120° to *W*90° by the silacyclobutane system.

[11] H. C. Brown and M. Borkowski, THIS JOURNAL, **74**, 1894 (1952), and other earlier papers on the elegant I-Strain hypothesis.

[12] Relative rate (k_2) for t-$C_4H_9Si(CH_3)_2H$ is 10^{-2}. Unpublished work of L. H. Sommer and W. P. Barie, Jr.

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RECEIVED MAY 23, 1957

THE PREMIXED OZONE-HYDROGEN FLAME[1]

Sir:

Mixing of pure ozone with combustible substances usually leads to self-ignition, explosion or detonation and *premixed* pure ozone–fuel flames have not been reported. They are interesting not only because of the higher enthalpy content of the O_3–fuel *vs.* the O_2–fuel system, but primarily because the combustion kinetics in the flame front of the O_3-systems can be expected to be substantially faster than for the corresponding O_2–systems.

We have described recently the combustion flame of ozone to oxygen.[2] We also found that pure ozone can be mixed with pure hydrogen at −78° and even at 20° and 1 atm. without explosion and with no, or practically no, reaction for several hours.

Pure ozone–hydrogen mixtures of any desired composition were prepared by mixing known volumes of the two gases. The mixtures were burned at −78° initial temperature using the same technique as before.[2] (The Reynolds numbers of all flames were below 2000.) The burning velocities were determined by the standard schlieren method. The same apparatus was used to measure the burning velocity of the H_2–O_2 system. The results are presented in Fig. 1. The experimental burning velocities at 195°K. initial temperature and 1.0 atm., were for 6.0, 12.0, 18.2, 18.5, 25.0 and 100.0 mole % O_3, respectively, 207 ± 5, 664 ± 57, 1290 ± 20, 1330 ± 30, 1680 ± 80 and 270 ± 7 cm./sec.

Mixtures of 94.0 to 75.0% H_2 (rest pure ozone) could be burned readily. These O_3–H_2 flames are brighter than the corresponding O_2 flames but like the latter their luminosity is low. The stoichiometric mixture, *i.e.*, 3.0 vol. H_2 + 1.0 vol. O_3, which could be appropriately called "super-knall gas," burns very rapidly at a velocity of 1680 ± 80 cm./sec., whereas "knall gas," classically considered the fastest burning gas mixture, burns at 610 cm./sec. or 1/2.75 as rapidly. In mixtures on the ozone-rich side of the stoichiometric point the flame front degenerates very rapidly to a detona-

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600) 1475. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] A. G. Streng and A. V. Grosse, THIS JOURNAL, **79**, 1517 (1957); see also *Proc. VIth International Symposium on Combustion*, Aug. 19–24, 1956; *Proc. International Ozone Conference*, Chicago, Ill., Nov. 28–30, 1956.

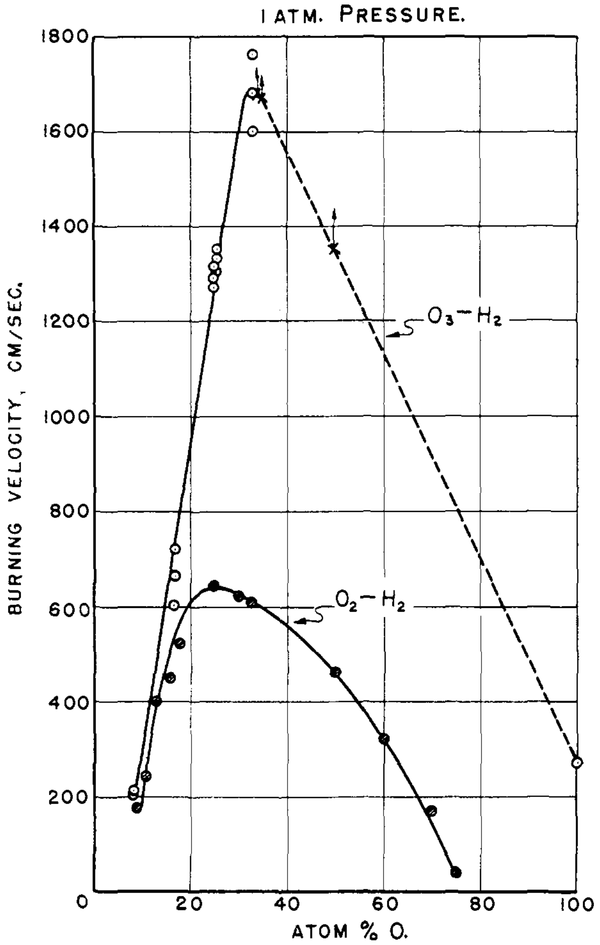

Fig. 1.—Burning velocities of $O_3 + H_2$ and $O_2 + H_2$ mixtures at 195°K. initial temperature and 1 atm. pressure.

tion front; it has not been possible as yet to burn such mixtures successfully.

The expected substantially faster burning velocity of the H_2–O_3 *vs.* the H_2–O_2 system has thus been proven experimentally. An intensive study of other O_3 flames is warranted.

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RECEIVED MAY 2, 1957

THE CONFIGURATION OF BASE-DENATURED β-LACTOGLOBULIN[1]

Sir:

It has been shown by Cannan, Palmer and Kibrick[2] that titration curves of β-lactoglobulin, in acid and neutral solutions at 25°, obey the Linderstrøm-Lang equation,[3] with a value for the electrostatic interaction factor *w* which is reasonable for a molecule of molecular weight 40,000. Above *p*H 10, however, the titration curves were found to be steeper, indicative of a considerably smaller value of *w*. A change in the properties of this protein near *p*H 10 is in accord with the finding of Groves, Hipp and McMeekin[4] that β-lactoglobulin becomes denatured near this *p*H. The titration curve above *p*H 10 thus represents the behavior of the denatured protein.

To investigate this behavior further, we have studied the dissociation of the phenolic groups of β-lactoglobulin, using the spectrophotometric method of Crammer and Neuberger.[5,6] The results are reported in the form of the logarithmic plot of Fig. 1.[7] The ordinate of such a plot represents the effective *pK* of the groups being titrated. According to any simple theory, such as the Linderstrøm-Lang theory, it should *increase* with increasing net negative charge because of the attractive force between this charge and the dissociating protons. In contrast to this prediction, Fig. 1 shows *p*H–log $\alpha/(1 - \alpha)$ to be essentially independent of charge. This same phenomenon is served in serum albumin,[8] for the phenolic and amino groups above *p*H 11, and for the carboxyl

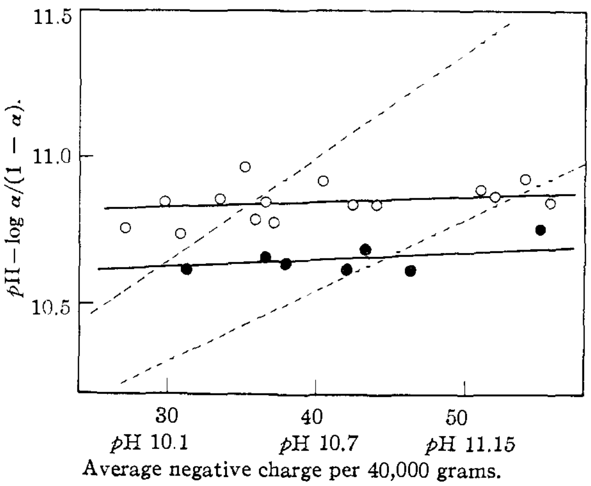

Fig. 1.—Titration of the phenolic groups of β-lactoglobulin at 25° and ionic strengths 0.08 (O) and 0.27 (●): the dotted lines show the predicted slopes for a compact sphere of molecular weight 35,000 to 40,000 at ionic strength 0.08 (upper line) and 0.27 (lower line). For a molecular weight of 17,500 the slopes of these curves would be reduced to about 0.6 of these values. The *p*H values are those at ionic strength 0.08; at ionic strength 0.27 the corresponding *p*H values are roughly 0.2 *p*H unit lower.

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(1) This work was supported by research grant G-1805 from the National Science Foundation and by research grant RG-2350 from the National Institutes of Health, Public Health Service.

(2) R. K. Cannan, A. H. Palmer and A. C. Kibrick, *J. Biol. Chem.*, **142**, 803 (1942).

(3) K. Linderstrøm-Lang, *Compt. rend. trav. Lab. Carlsberg*, **15**, No. 7 (1924).

(4) M. L. Groves, N. J. Hipp and T. L. McMeekin, THIS JOURNAL, **73**, 2790 (1951).

(5) J. L. Crammer and A. Neuberger, *Biochem. J.*, **37**, 302 (1943).

(6) C. Tanford and G. L. Roberts, Jr., THIS JOURNAL, **74**, 2509 (1952); C. Tanford, J. D. Hauenstein and D. G. Rands, *ibid.*, **77**, 6409 (1955).

(7) The charge at a given *p*H is based on a molecular weight of 40,000 and was taken from the titration curves of Cannan, *et al.*[2] Above *p*H 10.8 the charges represent an extrapolation of their results. Neither the assumed molecular weight nor the accuracy of the extrapolation affects our conclusions, for *p*H–log $\alpha/(1 - \alpha)$ is an experimental parameter independent of these variables, and we wish only to show that this parameter is virtually independent of charge.

(8) C. Tanford, J. G. Buzzell, D. G. Rands and S. A. Swanson, THIS JOURNAL, **77**, 6421 (1955).