

processes analogous to eq. 1 and 2 and combining the appearance potentials with the implied value of 140 ± 3 kcal. mole⁻¹ for $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}^+]$ and with thermochemical values for the radical heats of formation^{8,9} leads to molecular heats of formation for $(\text{CH}_3)_3\text{SiC}_2\text{H}_5$, $(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)_2$, $(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_3$, and $(\text{CH}_3)_3\text{SiCl}$ (column 4, Table I). To our knowledge there are no reported values for $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ and, of course, it cannot be obtained from the electron impact data since $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}]$ is unknown.

We have estimated $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ as -129 kcal. mole⁻¹ by means of the group equivalent method of Franklin¹⁰ using the heats of formation shown in column 4, Table I. We may use the same heats of formation to deduce the bond energy parameters required by Allen's calculational method.^{11,12} These parameters, which are consistent with those for other substituted paraffins,¹² yield a value for $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ that is within a few kilocalories per mole of that obtained by Franklin's method. Combination of our estimate of $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ with the appearance potential of $(\text{CH}_3)_3\text{Si}^+$ from $(\text{CH}_3)_6\text{Si}_2$ and with $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}^+]$ gives 7.2 e.v. for the ionization potential of the $(\text{CH}_3)_3\text{Si}$ radical or, equivalently, a value of -22 kcal. mole⁻¹ for $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}]$. This is expressed as bond dissociation energy of $(\text{CH}_3)_3\text{Si-X}$ in column 5 of Table I. The uncertainty in these dissociation energies which is estimated as ± 10 kcal./mole arises principally from the estimate of $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$.

Some indirect support for the ionization potential of the $(\text{CH}_3)_3\text{Si}$ radical (and therefore for the bond dissociation energies) may be derived from the following consideration: the appearance potential of $m/e = 57$ from $(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_3$, namely 11.88 e.v., is too high to reflect a simple dissociation process to $(\text{CH}_3)_3\text{C}^+$ and $(\text{CH}_3)_3\text{Si}$. If Stevenson's rule¹³ can be applied to organosilanes as well as to paraffinic hydrocarbons, one derives the following relationship of radical ionization potentials

$$I_z[(\text{CH}_3)_3\text{Si}] < I_z[(\text{CH}_3)_3\text{C}] = 7.42^{14}$$

Hence, lower limits for $D[(\text{CH}_3)_3\text{Si-X}]$ that are only 5 kcal. mole⁻¹ less than those in Table I are quite certain.

As found by previous investigators^{1,2} the Si-H and Si-Si bonds (particularly the latter) are considerably stronger than indicated by the thermochemical bond energies of 77.4 and 47.9 kcal. mole⁻¹, respectively.¹² Also, the dissociation energies of the C-Si bonds are of comparable magnitude to the corresponding C-C bonds although the dependence on alkyl type (R) is much less than for H₃Si-R bonds² or R-R bonds.¹⁵

The data in Table I indicate that in the gas phase the trimethylsilylium ion is sometimes somewhat easier to form from its molecular precursor than is the corresponding *t*-butylcarbonium ion. This is perhaps better seen in Table II in which we compare the difference between the heats of formation of the ions¹⁶ and

the molecular precursors for the corresponding carbon and silicon compounds.

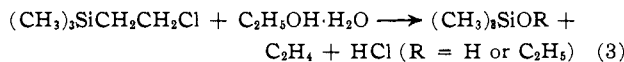
Interestingly enough only in the case of the chloride is there any really significant difference in the ease of formation of the trimethylsilylium and trimethylcarbonium ions, and in this case the large difference reflects the large dissociation energy of the Si-Cl bond.

In connection with possible significance of the data in Table II for reactions in solution, it is interesting to note the previous conclusion, based on various lines of

TABLE II
COMPARISON OF SILICONIUM AND
CARBONIUM IONIC STABILITIES

Compound	ΔH_f° [[$(\text{CH}_3)_3\text{Si}^+$] - $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si-X}]$, kcal. mole ⁻¹	Compound	ΔH_f° [[$(\text{CH}_3)_3\text{C}^+$] - $\Delta H_f^\circ[(\text{CH}_3)_3\text{C-X}]$, kcal. mole ⁻¹
$(\text{CH}_3)_3\text{SiH}$	200	$(\text{CH}_3)_3\text{CH}$	208
$(\text{CH}_3)_3\text{SiCH}_3$	209	$(\text{CH}_3)_3\text{CCH}_3$	217
$(\text{CH}_3)_3\text{SiC}_2\text{H}_5$	217	$(\text{CH}_3)_3\text{CC}_2\text{H}_5$	222
$(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)_2$	231	$(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$	226
$(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_3$	238	$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3$	236
$(\text{CH}_3)_3\text{SiCl}$	258	$(\text{CH}_3)_3\text{CCl}$	209

evidence, that reaction 3 proceeds *via* the siliconium ion-pair intermediate¹⁷, and the previously expressed conviction¹⁷ that trialkylsilicon cations, R_3Si^+ , and trialkylcarbon cations, R_3C^+ may, in certain circumstances, be of comparable stability relative to their precursors.



Acknowledgment.—This work was supported in part by the Petroleum Research Fund, Grant No. 833-A1, and in part by a fellowship grant from Dow Corning Corporation. We wish to thank the National Science Foundation for providing funds to aid in the purchase of the mass spectrometer.

(17) L. H. Sommer and G. L. Baughman, *J. Am. Chem. Soc.*, **83**, 3346 (1961).

WHITMORE LABORATORY
DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

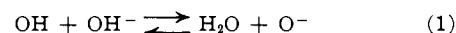
G. G. HESS
F. W. LAMPE
L. H. SOMMER

RECEIVED MAY 16, 1964

Pulse Radiolytic Determination of *pK* for Hydroxyl Ionic Dissociation in Water¹

Sir:

In several papers² the dissociation of OH has been assumed to account for radiation chemical results in alkaline solutions. The reaction most likely is



However, previous data did not permit calculation of the dissociation constant for OH, and values deduced

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

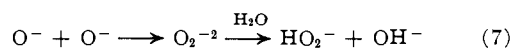
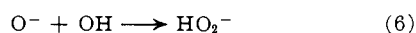
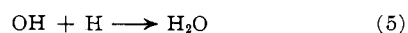
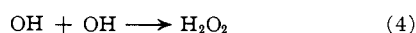
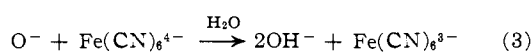
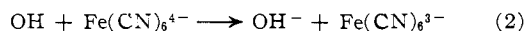
(2) (a) E. J. Hart, S. Gordon, and D. A. Hutchison, *J. Am. Chem. Soc.*, **75**, 6165 (1953); (b) *J. Chim. Phys.*, **52**, 570 (1955); (c) H. L. Friedman and A. H. Zeltmann, *J. Chem. Phys.*, **28**, 878 (1958); (d) G. Hughes and C. Willis, *Discussions Faraday Soc.*, **36**, 223 (1963).

(9) J. L. Franklin and F. W. Lampe, *Trans. Faraday Soc.*, **57**, 1449 (1961).
 (10) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).
 (11) T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959).
 (12) H. A. Skinner and G. Pilcher, *Quart. Rev. (London)*, **17**, 264 (1963).
 (13) D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).
 (14) F. P. Lossing, P. Kebarle, and J. B. DeSousa, "Advances in Mass Spectrometry," J. P. Waldron, Ed., Pergamon Press, London, 1959.
 (15) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth and Co., Ltd., London, 1958.
 (16) F. H. Field, and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

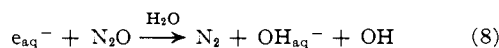
from theoretical speculations ranged from $pK = 7.3$ to 11.6 .^{2a} With this uncertainty, any pH effects in radiolyses in any pH range above 7 can be ascribed to OH dissociation.

We have used the pulse radiolysis technique^{3,4} to study the rate of ferrocyanide oxidation as a function of pH and thereby obtained a precise value of this pK at 23° .

By multiple reflection we achieved an optical path length of 80 cm. using a 4-cm. reaction cell.⁵ The long optical path was necessary, because low electron-pulse intensities favored the reactions with ferrocyanide (eq. 2 and 3) over the radical-radical reactions 4, 5, 6, and 7, and because the ferricyanide formed in reactions 2 and 3 was followed spectrophotometrically at 4200 \AA . where the ferricyanide extinction coefficient is only $1000 M^{-1} \text{ cm.}^{-1}$.



Ferrocyanide was usually present in such excess that a pseudo-first-order oxidation resulted. The hydrated electron absorption is about threefold that of ferricyanide at 4200 \AA . and also reacts rapidly with ferricyanide, H, and OH.⁶ To avoid these complications, e_{aq}^- scavengers were added. H atoms may also react with ferricyanide, but this effect can be neglected in neutral and alkaline solutions, since $G_{\text{H}} \simeq 0.2G_{\text{OH}}$, and since the amount of ferricyanide formed is much less than the initial ferrocyanide. (In acid solutions where $G_{\text{H}} \simeq G_{\text{OH}}$, the formation of ferricyanide was followed by a partial decay.) Either N_2O or CCl_4 or H^+ or air (O_2) was used to eliminate e_{aq}^- . With N_2O more OH is formed (in less than a microsecond in our experiments) by reaction 8,⁷ and the final optical density is



about two times that observed with the other electron scavengers. With CCl_4 the products of reaction are probably CCl_3 and Cl^- .

Experiments carried out with N_2O , CCl_4 , or air in neutral solution gave $k_2 = (1.1 \pm 0.2) \times 10^{10} M^{-1} \text{ sec.}^{-1}$. For N_2O or O_2 or CCl_4 , the optical density increased with a half-life of 1 to 2 $\mu\text{sec.}$, attaining a plateau. This indicated reduction of ferricyanide by O_2^- or CCl_3 could be neglected in our experiments. However, in $10^{-3} M \text{ HClO}_4$, although the initial change of density gave the same k_2 , a maximum optical density was reached followed by a partial decay.

(3) M. S. Matheson and L. M. Dorfman, *J. Chem. Phys.*, **32**, 1870 (1960).

(4) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

(5) J. Rabani, W. A. Mulac, and M. S. Matheson, submitted for publication.

(6) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963).

(7) F. S. Dainton and D. B. Peterson, *Nature*, **186**, 878 (1960).

The effect of pH on " k " is shown in Table I where " k " $[\text{Fe}(\text{CN})_6^{4-}]$ is defined as $[d \ln (D_\infty - D_t)]/dt$. These results indicate OH dissociates to O^- above pH 11 and that $k_2 \gg k_3$. Assuming that the reactions in (1) are so rapid that the equilibrium is maintained and that $k_2 \gg k_3$ (experiments support both assumptions)

$$\log [(k_2/'k'') - 1] = \text{pH} - \text{p}K$$

(see ref. 5 for an analogous case). Plotting the data of Table I in this function gives the pK for OH = 11.9 ± 0.2 .⁸ Values of " k " obtained at pH 12.5 and 13.1 with added CCl_4 (and no N_2O) give points on the same line; $1.02 \times 10^{-2} M \text{ Ba}(\text{ClO}_4)_2$ or $0.30 M \text{ Na}_2\text{SO}_4$ in N_2O solutions did not affect the agreement of points obtained either in neutral solutions or at pH 12.5. These results show that the change in " k " with pH is due to the OH^- concentration and not to the added Ba^{+2} , Na^+ , or N_2O .

TABLE I
EFFECT OF pH ON " k " IN
AQUEOUS N_2O -FERROCYNIDE SOLUTIONS

Initial [$\text{Fe}(\text{CN})_6^{4-}$], μM	D_∞^a	pH ^b	" k " ^c
25	0.227	Neutral	1.2
48	0.310	Neutral	1.06
71	0.255	11.94	0.49
110	0.310	12.10	0.36
360	0.320	12.57	0.19
130	0.345	13.07	0.071
420	0.330	13.08	0.065
1100	0.345	13.07	0.063

^a Final optical density with 80-cm. light path. D_∞ is proportional to the intensity of the 0.4- $\mu\text{sec.}$ pulse to the extent that G values are constant with pH. ^b The pH was adjusted with NaOH containing 5 mole % $\text{Ba}(\text{OH})_2$. Experiments at 5780 \AA . showed no absorption due to carbonate radicals. ^c In units of $10^{10} M^{-1} \text{ sec.}^{-1}$; corrections for ferrocyanide depletion and second-order reactions were small and were omitted.

Finally, when low concentrations of $\text{Fe}(\text{CN})_6^{4-}$ and high pulse intensities ($\sim 1.3 \times 10^{-5} M \text{ OH}$) are used in N_2O solutions, the radical-radical reactions compete with reaction 2, and this competition determines the final optical density. Computer fitted curves gave $2k_4 = 1.2 \times 10^{10}$ and $2k_7 \sim 2 \times 10^9 M^{-1} \text{ sec.}^{-1}$. Our value of $2k_4$ is in satisfactory agreement with previous work.⁹

Masri and Haissinsky¹⁰ find complications in *prolonged* irradiation of air-saturated ferrocyanide solutions, but assume OH always oxidizes ferrocyanide to ferricyanide. Thus, these complications should not occur in our experiments, and our evidence supports this conclusion.

We are continuing these experiments to obtain more precise values of $2k_4$ and $2k_7$, and also to investigate a weak absorption at 2600 \AA . formed during the pulse with and without N_2O but without added ferrocyanide. Possible absorbing species are OH in neutral and O^- in alkaline solution. The time dependence of this absorption in alkaline solutions is complex.

(8) J. W. Boag, private communication, finds $pK = 12$.

(9) (a) H. A. Schwarz, *J. Phys. Chem.*, **66**, 255 (1962); (b) H. Fricke and J. K. Thomas, *Radiation Res. Suppl.*, **4**, 35 (1964).

(10) E. Masri and M. Haissinsky, *J. Chim. Phys.*, **60**, 397 (1963).

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60440

JOSEPH RABANI
MAX S. MATHESON

RECEIVED JUNE 6, 1964