



Moderation of Hot Methyl Radicals in Photolysis of Methyl Iodide

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overlap integrals involving the carbon 3d orbitals must vanish. The Slater effective nuclear charge is, however, only zero for the negative carbon atom C⁻ appropriate to the bimolecular substitution transition state. In the carbonium-ion rearrangement transition state and metal alkyl compounds the carbon atom that is being considered is neutral, and for this case Slater's rules give $Z_{eff} = 1$. In any case it must be emphasized that Slater's rules are only approximate. It has been shown recently⁵ that they may be particularly inaccurate in rather similar cases to those under consideration, such as, for example, the 3d orbitals of the phosphorus atom in PCl₅, for which it appears that the value of Z_{eff} given by Slater's rules is appreciably too small. The estimation of a reasonable value for the effective nuclear charge in the type of compound we are considering is a matter of some difficulty (this will be further discussed in a later paper) but there seems to be little justification at present for concluding that overlap integrals involving carbon 3d orbitals are necessarily inappreciable, and that therefore the carbon atom cannot utilize 3d orbitals for bond formation.

¹ R. J. Gillespie, J. Chem. Soc. **1952**, 1002. ² H. H. Jaffé, J. Chem. Phys. **21**, 1893 (1953). ⁴ Jaffé's further objection that in the compounds of phosphorus and sulfur so far considered there is a complete transfer of one or two electrons from the phosphorus or sulfur atom to the attached atoms, whereas this does not occur in carbon compounds, is not sound. It may be assumed that a transfer of one or two electrons occurs in these compounds of phosphorus and sulfur, and their structures may then be described in terms of *3p*-hybrid orbitals and ionic-covalent resonance without involving the use of *3d* orbitals at all. If, however, *spd* hybrid orbitals are used in the description of these structures than all the valency electrons of phosphorus and sulfur must be regarded as being involved in covalent bonding and none of them can be considered to have been completely transferred to the attached atoms.

4 J. C. Slater, Phys. Rev. 36, 57 (1930).
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Moderation of Hot Methyl Radicals in Photolysis of Methyl Iodide*

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HE study of the photolysis of methyl iodide vapor by Schultz and Taylor¹ was interpreted to show that methane production is by a hot radical mechanism. Since the energy of a light quantum of 2537A is approximately 50-60 kcal greater than the C-I bond strength in methyl iodide and the masses of the radical and atom are so different, the methyl radical produced in the primary process must have most of this excess energy, largely as kinetic energy. Production of methane in this system is proposed to occur mainly in early, hot collisions of the energetic methyl radicals with methyl iodide. Two important consequences of this mechanism are a temperature-independent rate of methane production, found by Schultz and Taylor and moderation of the rate of methane production by inert gases added, shown qualitatively for carbon dioxide by Schultz and Taylor. However, it is possible that this substance might exert a specific chemical effect other than moderation. We have shown² that an analogous mechanism may be applied to the photolysis of hydrogen iodide and have also investigated methyl-iodide photolysis to test further and to develop the hot radical hypothesis. We have photolyzed methyl iodide with light from a Hanovia SC2537 lamp, filtered through Corning 7910 glass. Noncondensable products have been analyzed with a Consolidated 21-103A mass spectrometer. At constant light absorption, we find the rate of methane production to be experimentally independent of temperature over the range 25-100°C in pure methyl iodide and in methyl iodide plus neon at a pressure six times that of the methyl iodide.

We have examined the effect of moderating gases on the rate of methane production in methyl iodide at constant partial pres-



FIG. 1. Rate of methane production in the presence of added inert gases (M). Legend: open circle, neon; triangle, argon; square, helium; crossed open circle, carbon dioxide (all in 7910 glass); crossed closed circle, carbon dioxide in quartz.

sure of 100 mm Hg, as shown in Fig. 1. Here we find a regular decrease in the rate of product formation with decreasing ratio of methyl iodide to moderator. In all cases, it appears that the rate approaches zero at infinite dilution by moderator. We also note that, if fused silica is used instead of Corning 7910 glass (which cuts off at approximately 2200A), carbon dioxide is not as effective as a moderator. This may be because of formation of still more energetic radicals by absorption of the 1849A mercury line of the resonance lamp.

We believe that the comparable effects of the various moderators rules out the possibility of a specific chemical effect and strengthens the hot radical hypothesis. Analysis of other products of this reaction and of reaction of hot methyl radicals with various substrates will be reported later.

* Taken from the Ph.D thesis of Frank P. Hudson. Work supported in part by U. S. Atomic Energy Commission under contract At (11-1)-38.
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Crystal Structure of Silanols and their **Infrared** Spectra

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RYSTAL structures of diethylsilanediol¹ and diphenylsi-→ lanediol² have been previously reported. We have now added diallylsilanediol (C3H5)2Si(OH)2,3 bis-(dimethylhydroxysilyl) methane OH(CH₃)₂SiCH₂Si(CH₃)₂OH,⁴ and tetramethyldisiloxanediol-1,3 OH(CH₃)₂SiOSi(CH₃)₂OH in our study on crystal analysis. Their crystallographic data are given in Table I. The molecular arrangement of diallylsilanediol is similar to diethylsilanediol, while the diols having OH groups at both ends of their molecules such as OH(CH₃)SiCH₂Si(CH₃)₂OH form a chain

FABLE	I.

	$(C_{3}H_{7})_{2}\mathrm{Si}(\mathrm{OH})_{2}$	$(OH(CH_3)_2Si)_2O$	(OH (CH ₃) 2Si) 2CH
Density	1.105(10°C)	1.118(16°C)	1.078(20°C)
System	Monoclinic Flat prismatic	Monoclinic Needle	Orthorhombic Needle
Unit cell	a = 14.59 kX. b = 4.94 c = 13.37 $\beta = 114^{\circ}30'$	a = 21.28 kX. b = 5.86 c = 8.46 $\beta = 111^{\circ}00'$	a = 14.50 kX. b = 11.31 c = 6.14
Space group	$C_{2h}^{b} - P_{21}/a$	$C_{2h^5} - P2_1/a$	$D_{2^4} - P2_{12_12_1}$
Moles in a unit cell	4	4	4



structure against the layer structure in the case of alkylsilanediols. However, it may be said that all these silanols take a similar structure from the viewpoint that the molecular chains linearly joined by two OH groups of each molecule are gathered side by side and parallel to an axis according to their own lateral interactions. As regards these strong hydroxyl associations, the relation between the arrangement of OH groups and the infrared absorption spectra of diethylsilanediol has been examined.* The nearest OH...OH distances in diethylsilanediol are 2.56 and 2.64A, and the others are longer than 3.5A.

On the basis of these inter-hydroxyl distances, it is proposed that the formula for the hydrogen bondings is of types 1 or 2.5 The infrared absorption spectra of the O-H bond were shown in Fig. 1. Curve 1 shows only a broad band with a maximum at 3.1 μ , while the absorption maximum expected from the relation between O-HO distances and shifts of O-H stretching frequency reported by Kuhn⁶ and Lord,⁷ must be at 4.1μ in the case of diethylsilanediol.

This indicated that the type 2, which has the same numbers intra- and inter-molecular hydrogen bond with different O-H stretching frequency, cannot exist in crystal. The O-H stretching vibration in Si-OH of afwillite, in which there are both a hydrogen bond and a nearly free O-H bond, was observed at 3.03, 2.95, and 3.3~4.0µ by Megaw.8

From these facts, it is reasonable to suppose that the molecular chain in crystalline silanol is formed by hydroxyl association as shown by type 1, in which there is only a kind of O-H bond. In its dilute solution, the free O-H vibration at 2.72, and 2.77μ appears, and these figures are similar to those for the absorption of an orgainc alcohol solution. This shows that the molecules of





silanol in solution are not associated with each other in the way of type 3 expressing the pentavalent coordination of the silicon atom, but are linked by a hydrogen bond of type 1 or 2, as predicted in the case of tri-ethylsilanol solution by Grubb and Osthoff.⁹ It can be considered as a property of the hydroxyl group in silanols, which may throw light on the study of their physico-chemical behavior.

A more detailed study on the hydroxyl bond in various types of crystalline silanols such as tetramethyldisiloxanediol-1,3 etc. has now been progressing.

We wish to offer our sincere thanks to Dr. W. L. Roth and his co-workers who kindly sent us their recent papers about silanols, and encouraged us.

We are grateful for the kindness of Mr. T. Kanzawa and Mr. T. Okawa in the taking of the infrared absorption spectra.

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Proton Magnetic Resonance Experiment on a Single Crystal of Oxalic Acid Dihydrate, $(COOH)_2 \cdot 2H_2O$

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HE crystal structure of oxalic acid dihydrate has already been determined rather precisely by many investigators¹ (space group, $C_{2h}^5 - P2_1/a$; Z=2). The atomic positions are shown in Fig. 1. No information about the positions of the hydrogen atoms, however, have been given by x-ray analyses.

Richards and Smith² made a proton magnetic resonance experiment on a polycrystal of this acid hydrate and proposed a proton configuration for the interpretation of the second moments of the absorption lines. But their suggestion involves, as they stated, ambiguities about the distance and the direction of the lines joining protons.

We have carried out a proton magnetic resonance experiment with a single crystal at a frequency of 6.1 Mc/sec. When the crystal was rotated about the b axis, the line shape was observed at a particular angle, which was composed of seven components, not well resolved owing to the broadness of each component line. Since it is known that, in the case of b-axis rotation, proton magnetic resonance lines for each of four molecules in the unit cell coincide with each other, this appearance of seven lines suggests the existence of a three-proton system in the crystal. We made further measurements at various other orientations of the crystal. Although, in general, lines expected from the three-proton interaction are not resolved clearly, the most separated components were well resolved in some cases. Assuming suitable configurations of three protons, the resonance line positions and relative intensities are calculated for various orientations of the crystal, using the formula of Andrew and Bersohn.3 Satisfactory agreement with the experimental results is obtained, when it is assumed that the triangle composed of three protons has the sides of 1.65, 1.92, and 2.30A, and the angles between the a axis and the projections of the sides of 1.65 and 1.92A onto the ac place are \sim 51° and \sim 28°, respectively. These two sides make angles of \sim 57.5° and $\sim 90^{\circ}$ with the *b* axis.

Now the position of the three-proton triangle in the lattice will be considered. Firstly, the proton-proton distance between