

846. *Organosilicon Compounds. Part VII.\* A Molecular Complex between Iodine and Tricyclohexyliodosilane.*

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The existence is reported of a 1 : 1 molecular complex between iodine and tricyclohexyliodosilane.

THE colour of solutions of iodine in trialkyliodosilanes is similar to that of iodine in methyl iodide, which suggested to us that organosilicon iodide-iodine complexes might be present (cf. Keefer and Andrews, *J. Amer. Chem. Soc.*, 1952, **74**, 1891; Hastings, Franklin, Schiller, and Matsen, *ibid.*, 1953, **75**, 2900). Mixtures of iodine and trimethyliodosilane showed significant light absorption at 260—340  $m\mu$  in both hexane and carbon tetrachloride, with a maximum at 270—290  $m\mu$  in the former solvent, but instability of the iodide prevented quantitative study. Mixtures, in hexane, of iodine and the relatively stable tricyclohexyliodosilane showed markedly enhanced absorption below 360  $m\mu$ , with a flat maximum at 284—292  $m\mu$  (probable peak  $\sim$ 289  $m\mu$ ), and the absorption figures at 290  $m\mu$  for various concentrations were analysed by Benesi and Hildebrand's method (*ibid.*, 1949, **71**, 2703). A straight line was obtained when  $[I_2]/D$  was plotted against  $1/[A]$ , where  $[I_2]$  and  $[A]$  are the respective *molar* concentrations of iodine and tricyclohexyliodosilane (cf. Hastings

\* Part VI, *J.*, 1953, 3148.

*et al., loc. cit.*), and  $D$  is the optical density of the solution for a 1-cm. light-path (after correction for the absorption of free iodine present). Thus the absorption arises from a 1 : 1 molecular complex, and the equation

$$[I_2]/D = 1/K\epsilon_c A + 1/\epsilon_c \dots \dots \dots (1)$$

applies, where  $\epsilon_c$  is the molecular extinction coefficient of the complex, and  $K$  is the equilibrium constant of the equilibrium  $I_2 + R_3SiI = R_3SiI, I_2$  at 18°.

The reciprocal of the intercept on the  $[I_2]/D$  axis shows  $\epsilon_c$  to lie between 17,000 and 29,000, with a most probable value of 22,000, and insertion of this figure in equation (1) gives the value of  $K$  at each concentration. Use of absorptions at 300 or 320 in place of those at 290  $m\mu$  gives similar results.

$10^3 \times [R_3SiI], M$	1.081	2.569	5.110	7.098	8.184	12.66	14.14	16.38	25.34	32.77
$10^3 \times [I_2], M$ ...	2.05	1.025	2.050	0.492	0.167	0.512	0.984	0.333	0.974	0.666
$10 \times D$ .....	3.82	4.60	1.758	5.94	2.32	10.70	22.00	8.50	36.85	30.15
$10^2 K$ .....	79	81	79	82	82	82	80	80	82	80

In stability the complex falls between the *isopropyl* iodide-iodine and the *tert.*-butyl iodide-iodine complex ( $K = 0.44$  and  $1.33$ , respectively; Keefer and Andrews, *loc. cit.*). The stability depends largely on the electron density on the iodine atom of the halide, and while the Si-I bond should be inherently more polar than the C-I bond, because of the more electropositive character of silicon, the stabilization of secondary and, particularly, tertiary alkylcarbonium ions by hyperconjugation will compensate for this. Siliconium ions, which are less stabilized by conjugation (Gilman and Dunn, *ibid.*, 1950, 72, 2178; Gilman and Wu, *ibid.*, 1953, 75, 3762) are presumably less stabilized by hyperconjugation.

Organosilicon iodide-iodine complexes account in part for the absorption maxima at 270—290  $m\mu$  which develop in mixtures of triethyl- or *triisobutyl*-silane in carbon tetrachloride, presumably as the reaction  $R_3SiH + I_2 \longrightarrow R_3SiI + HI$  proceeds (Deans and Eaborn, *Research*, 1952, 5, 592). The rest of this absorption, and a maximum of lower intensity at 350—360  $m\mu$ , seem to come from the tri-iodide ion, which has peaks at 352 and 289  $m\mu$  in water and at 363  $m\mu$  in carbon tetrachloride containing acetone (Custer and Matelson, *Analyt. Chem.*, 1949, 21, 1005; Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1950, 72, 2273). Mixtures of iodine and a little hydrogen iodide in carbon tetrachloride or hexane showed peaks at 280—290 and 350—360  $m\mu$ , but higher concentrations of hydrogen iodide caused a cloudiness, and after removal of this with alumina the peaks were absent, although hydrogen iodide and iodine were still present. Presumably the solvents, although carefully dried, had picked up traces of water; when these were removed by excess of hydrogen iodide and alumina, tri-iodide ion could not exist in the system. In the *tricyclohexyl*iodosilane-iodine system low absorption in the 360- $m\mu$  region showed that formation of tri-iodide ion by water was insignificant. The theory of Hastings *et al.* (*loc. cit.*) would predict an absorption maximum of  $\sim 240$   $m\mu$  for an  $HI, I_2$  complex, an ionization potential of 10.33 ev being assumed for hydrogen iodide. The theory indicates an ionization potential of  $\sim 9.2$  ev for *tricyclohexyl*iodosilane (see also McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, 21, 66).

*Absorption Spectrum of Tricyclohexyliodosilane.*—The absorption of trimethyliodosilane in hexane is complicated by decomposition, but there is no maximum above 220  $m\mu$ ; at 240  $m\mu$   $\epsilon$  is  $< 40$ . *Tricyclohexyl*iodosilane in hexane has  $\epsilon_{max.} = 2800$  at 209  $m\mu$ . This is surprisingly different from the absorption of alkyl iodides; *tert.*-butyl iodide, for example, has  $\epsilon_{max.} = 590$  at 270  $m\mu$  (Haszeldine, *J.*, 1953, 1764). If the absorption in both cases arises from photodissociation to give the same excited iodine atom, the shift of  $\lambda_{max.}$  is greater than expected from consideration of the empirical energies of Si-I and C-I bonds (51.1 cal. and 45.5 or 57 cal., respectively; Pauling, "Nature of the Chemical Bond," Ithaca, New York, 2nd Edn., 1940, p. 53; Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, Oxford, 1950, Vol. I, p. xxxi), and may even be in the wrong direction. Bond-dissociation energies, which would be more significant, are not available for Si-I bonds. In spite of their lower absorption in the nearer ultra-violet, organosilicon iodides liberate iodine much more rapidly in sunlight than does, say, methyl iodide.

In line with the behaviour of tricyclohexyliodosilane, triethylbromosilane has no maximum above 200  $m\mu$  ( $\epsilon$  is  $<5$  at 210  $m\mu$ , and  $<20$  at 200  $m\mu$ ), whereas methyl bromide has  $\epsilon \sim 100$  at 217  $m\mu$  and  $\epsilon_{\max}$  182 at 204  $m\mu$  (Fink and Goodeve, *Proc. Roy. Soc.*, 1937, *A*, 163, 592).

## EXPERIMENTAL

*Tricyclohexyliodosilane*.—This compound, m. p. 97—98°, was prepared by Nebergall and Johnson's method (*J. Amer. Chem. Soc.*, 1949, 71, 4022) but with recrystallization from light petroleum at 0°.

*Spectra*.—A Unicam S.P. 500 spectrophotometer was used.

Hexane, which was free from light-absorbing impurities, was boiled with calcium hydride and distilled from this substance. "AnalaR" carbon tetrachloride was dried over phosphoric oxide and distilled from this substance.

The following data enable the absorption curve of tricyclohexyliodosilane in hexane to be drawn :

$\lambda$ ( $m\mu$ )	.....	270	260	250	240	230	220	216	212	209	206	204	200
$\epsilon$	.....	0	~3	20	130	590	1640	2205	2780	2825	2725	2535	2150

The absorption obeyed Beer's law in the range studied ( $10^{-2}$ — $10^{-3}M$ ). Free iodine present was less than could be detected by its absorption at 520  $m\mu$ .

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