Raman Spectrum of Tetraethyl Orthosilicate

Jules Duchesne

1.2 times) greater than the rate of exchange. The latter was measured by the increase in abundance of the ion $m/e = 57$, due to ionization of $CH_2D-CH=CH-CH_3$ in the mass spectrometer. Activation energies for isomerization and exchange were found to be 7.8 ± 0.7 kcal. and 7.1 ± 0.7 kcal., respectively. The essential equality of these two rates supports the idea that each isomerization is accompanied by an exchange; e.g.,
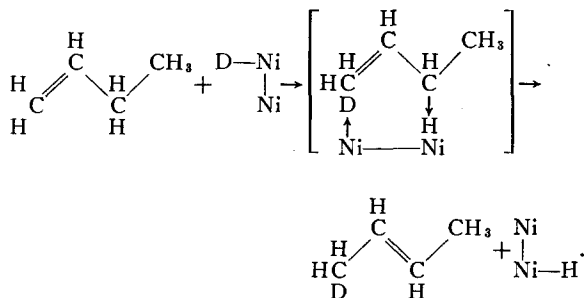
As the reaction progresses, the deuterium is diluted with protium, and the apparent exchange rate decreases. At the same time the isomerization rate increases, as evidenced by the observation that in the presence of pure protium at 100°C, the isomerization rate constant is ten times that in the presence of deuterium. This may account for the difference between our results and those of Twigg, who reported an isomerization rate six times the deuterium exchange rate.[2]

Initially, the rate constant for the second deuterium atom exchanged into the butene molecule is approximately one-fifteenth that of the first deuterium atom. This was measured by observing the rate of increase in abundance of the $m/e = 58$ ion. On the basis of the "hydrogen-switch" theory, the second deuterium atom should be introduced primarily by 2-butene reverting to 1-butene to form (I) $CHD=CH-CHD-CH_3$ or (II) $CH_2D-CHD-CH = CH_2$. The observed difference in the above rate constants corresponds roughly to the value that one would predict from the observed equilibrium concentration of 2-butene, i.e., 95.0 ± 2.0 percent and 93.0 ± 2.0 percent at 93 and 130°C, respectively. The mass spectral data indicated provisionally that approximately two-thirds of the butene-d_2 molecules had the (I) structure. The significance of this observation is being investigated further.

Initially, the rate constant for deuterium-induced isomerization was about 20 times that of deuterium addition; while the rate of protium-induced isomerization (activation energy 5.0 ± 0.5 kcal.) was approximately twice that of protium addition (activation energy 2.0 ± 0.3 kcal.). This suggests that the addition and the isomerization-exchange mechanisms are different.

More nearly complete details of this study will be published at a later date.

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[1] J. Turkevich and R. K. Smith, J. Chem. Phys. 16, 466 (1948).
[2] G. H. Twigg, Proc. Roy. Soc. A178, 106 (1941).
[3] For a comprehensive presentation of early work on this subject see the Faraday Society's general discussion on hydrocarbon chemistry, Trans. Faraday Soc. 35, 806 (1939).

Raman Spectrum of Tetraethyl Orthosilicate

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THE analysis of the Raman spectra of substances like tetraethyl orthosilicate $Si(OC_2H_5)_4$ seems of some general interest, mainly on account of the SiO_4 group which they possess in common with other molecules such as the siloxanes. The purpose of the present note is to report briefly our investigations on the vibration spectrum of this compound and to discuss the skeletal frequencies of SiO_4 and C_2H_5.

Our results for tetraethyl orthosilicate in the liquid state, together with the rough relative intensities, are listed in the following table. Diffuse and sharp lines are designated, respectively, by d and s, and the exciting mercury lines are referred to by the letters $e = 4358$A and $k = 4047$A. The spectrograph was a "Huet" glass prism instrument giving a dispersion of about 20A/mm in the region investigated. The mean error of our measurements is about ±2 cm^{-1} for most lines. Microphotometer records were made, and the weakest diffuse lines were measured on these with errors of about ±10 cm^{-1} for the three lower frequencies.

2975 (5,s) (e,k)	1392 (2,sd) (e,k)	280 (o,dd) (e)
2929 (7,s) (e,k)	1293 (5,sd) (e,k)	236 (o,dd) (e).
2888 (6,s) (e,k)	1087 (6,d) (e,k)	
2867 (4,sd) (e,k)	970 (2,d) (e,k)	
2766 (1,d) (k)	932 (2,s) (e,k)	
2718 (1,sd) (e,k)	810 (2,dd) (e,k)	
1483 (6,s) (e,k)	790 (2,dd) (e,k)	
1456 (6,sd) (e,k)	652 (5,s) (e,k)	
1443 (5,sd) (e,k)	318 (o,dd) (e)	

The intense lines observed at 2975, 2929, 2888, and 2867 cm^{-1} must correspond to C—H valency vibrations. We may correlate them, respectively, with $\nu_\perp(CH_3)$, $\nu_{||}(CH_3)$, $\nu_\perp(CH_2)$, and $\nu_{||}(CH_2)$, in good quantitative agreement with the assignments made for ethers.[1] The C—H deformation frequencies are probably to be identified with the lines at 1392, 1443, 1456, and 1483 cm^{-1}, which are also intense. We suggest that the lines 1443 and 1483 cm^{-1} may be due to a splitting of the doubly degenerate $\delta_\perp(CH_3)$ vibration, as has been assumed in the interpretation of the spectrum of methyl alcohol,[2] whereas 1392 and 1456 cm^{-1} may both be assigned as either $\delta_{||}(CH_3)$ or $\delta(CH_2)$. The intense line at 1293 cm^{-1} can be associated with an ethyl rocking frequency, and the weak one at 790 cm^{-1} may perhaps arise from a methylene rocking vibration, as suggested by recent observations made with paraffins.[3] 2718 and 2766 cm^{-1} are probably the first overtones of the fundamentals 1390 and 1443 cm^{-1}. Three lines with frequencies 810, 932, 970 cm^{-1} are thus left for consideration; the others will be interpreted as vibrations of the SiO_4 group. These are probably fundamentals corresponding to valency vibrations of C—C—O. Any further attempt at making an exact assignment of these lines would be speculative, until the normal modes have been analyzed in detail.

Assuming that the SiO_4 group is tetrahedral and behaves independently from the rest of the molecule, four vibrations should appear. Thus by analogy with the behavior of the fundamental frequencies of tetrahedral pentatomic molecules, we should expect $\nu_3 > \nu_1 > \nu_4 > \nu_2$, where ν_1 is the non-degenerate symmetrical vibration, ν_2 is the doubly degenerate one, and ν_3 and ν_4 are the triply degenerate ones. The 652-cm^{-1} intense line which appears also in methyl silicate, where it is strongly polarized,[4] remains, according to preliminary results obtained by Thosar and Bapat,[5] practically constant in a series of homologous molecules. It must presumably correspond to ν_1. If so, ν_3 is to be identified with 1087 cm^{-1} and ν_4 and ν_2 are to be chosen among 236, 280, 318 cm^{-1}. The value obtained for ν_3 is in close agreement with that found for methyl-polysiloxanes,[6] which give rise to an antisymmetrical stretching vibration of the Si—O bonds at 1050 cm^{-1}. Deformation vibrations involving the Si—O bond occur in the vicinity of 400 cm^{-1} in the Raman spectrum of crystalline quartz.[7] This too supports our assignment of ν_2 and ν_4 and accounts for a certain similarity of the Si—O bonds in these different kinds of molecules.

If we suppose that a valence force field is able to represent the vibrations of SiO_4, two relations between the frequencies and the masses of atoms result. The following assignment,

$$\nu_1 = 652 \text{ cm}^{-1}, \ \nu_2 = 236 \text{ cm}^{-1}, \ \nu_3 = 1087 \text{ cm}^{-1}, \ \nu_4 = 280 \text{ cm}^{-1},$$

verifies the relations satisfactorily. The values of the stretching and deformation force constants deduced are 5 and 0.2×10^5 dynes/cm, respectively; they enable one to recalculate the observed frequencies with a maximum error of ten percent. This result would not be appreciably modified by an alternative assignment for ν_2 and ν_4.

On the whole, the consistency for the valence force system is rather satisfactory, and the reasonable values obtained for the force constants give some evidence of the symmetrical tetrahedral character of SiO_4. Further, the Si—O bond distance seems to be the same in the silicate as in the polysiloxanes, as is shown by the equality of the force constants.[6] It would seem that the C_2H_5 and SiO_4 groups are relatively independent and behave quite normally so far as the intensity and magnitude of their frequencies are concerned.

A full account of this work will be published later.

We are very indebted to Dr. D. M. Simpson who has read the manuscript and kindly revised the English.

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