

Mass Spectrometric and InfraRed Study of Rates of Deuterium Exchange, Isomerization, and Hydrogenation of the nButenes

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pairs of C_1 cages forming *intramolecular* parallel intergrowths on cube faces, rather than a single C_2 cage.⁷ Either of the first two suggestions places cyclic hexapeptides carrying closely packed *R*-substituents on antipodal faces normal to the trigonal axis, which interact in Patterson space to yield a local maximum at rather more than 12Å from the origin which may be compared with the maximum in the region *C* which falls at $z \sim \frac{2}{3}$, i.e., at 13.6Å from the origin.

* This work is supported by the Office of Naval Research under Contract N8onr-579.

¹ Crowfoot and Riley, *Nature* **144**, 1011 (1939).

² Crowfoot, *Chem. J.* **G15**, 215 (1946).

³ D. Wrinch, *Proc. Roy. Soc. London* **A161**, 505 (1937).

⁴ D. Wrinch, *Science* **107**, 445 (1948).

⁵ Oncley, *Science* **106**, 509 (1947).

⁶ D. Wrinch, *Phil. Mag.* **26**, 325 (1938).

⁷ D. Wrinch, *J. Am. Chem. Soc.* **60**, 2005 (1938).

Vibrational Bands Measured with a Thallium Bromide-Iodide Prism

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August 11, 1948

IN recent papers¹ the writer has shown the method of calibration and use of the thallium bromide-iodide prisms for measurements to 40 microns. It was also found that polyethylene and polystyrene, in thin layers, are highly transparent in the 24- to 40-micron region and are well suited for window materials.

TABLE I. List of observed bands.

Substance	Wave-length (μ)	Wave number (cm^{-1})
Trichloroethylene	22.3	448
	25.9	386
	36.0	278
Tetrachloroethylene	23.4	427
	24.8	403
	28.8	347
	34.8	287
Benzene	24.8	403
Isobutylbenzene	22.5	444
	23.7	422
	24.9	402
	28.9	346
Methylene chloride	34.9	286
Carbon tetrachloride	30.5	328
	32.3	310
Bromoform	23.1	433
	25.8	388
	26.4	379
1,3,5-trimethylbenzene	30.0	333
	36.4	275
S-tetrabromoethane	22.4	446
	25.1	398
	35.5	282
Toluene	28.7	348
Chloroform	27.1	369
Carbon disulfide	25.2	397

A study has been made of the absorption spectra of about 30 substances in the long wave-length region, and bands have been found for molecules containing C=S, C-Cl, C-Br, and C-I and other atomic groups. In nearly all cases, cells of 0.4 mm or more in thickness are necessary for the observation of the bands. In Table I are given the wave-lengths and the frequencies of the observed bands for a selected group of substances.

Some of these frequencies have been predicted in studies of the molecular structure of these molecules.² In the gaseous state the bands are broad, and the regions of maximum absorption are not so clearly defined. The CS_2 band, as measured in the vapor state at 25.2μ , is strong and is suitable for checking the calibration of the instrument. The absorption band of CCl_4 at 32.3μ has been observed in the vapor. Propane has a band in the region of 26μ and some general absorption beyond 30μ . A detailed discussion of these absorption bands, as well as those of other substances comprising a total of thirty, will be given in a publication now in preparation.

¹ E. K. Plyler, *J. Chem. Phys.* **15**, 885 (1947), *J. Opt. Soc. Am.* **38**, 664 (1948).

² W. J. Taylor and R. S. Pitzer, *J. Research Nat. Bur. Stand.* **38**, 1 (1947); G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

Mass Spectrometric and Infra-Red Study of Rates of Deuterium Exchange, Isomerization, and Hydrogenation of the *n*-Butenes

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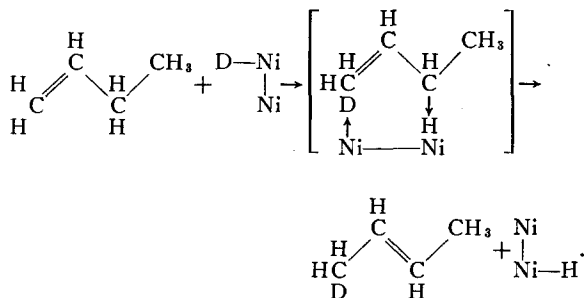
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August 18, 1948

MUCH work has been reported on the nickel-catalyzed deuterium exchange, isomerization, and hydrogenation of the *n*-butenes. The use of mass spectrometric and infra-red analyses to determine the rate constants for the initial stages of these processes seemed to us to offer certain advantages over methods used in previous studies. In particular, mass spectral data should give information on the rates of exchange and addition as well as the position of the exchanged deuterium atom in the molecule. The "hydrogen-switch" mechanism recently proposed by Turkevich and Smith¹ for isomerization and tritium exchange is supported by our results. In certain respects we differ from the results of earlier studies by Twigg² and others.³

The reactions were carried out with equimolar quantities of hydrogen and olefin in a 400-cc Pyrex vessel containing an 80-cm length of 0.25-mm diameter nickel wire activated by heating alternately in oxygen and hydrogen. Rates of formation of deuterobutenes and of butane were observed by mass spectrometric analysis. Infra-red absorption at 925 cm^{-1} was used to follow the rate of isomerization of 1-butene to 2-butene.

During the initial stages of the reaction between deuterium and 1-butene, in the temperature range 93 to 130°C , the rate of isomerization was only slightly (1.0 to

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 $\text{CH}_2\text{D}-\text{CH}=\text{CH}-\text{CH}_3$ 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) $\text{CHD}=\text{CH}-\text{CHD}-\text{CH}_3$ or (II) $\text{CH}_2\text{D}-\text{CHD}-\text{CH}=\text{CH}_2$. 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.

* National Institute of Health Research Fellow, 1947-48.

¹ J. Turkevich and R. K. Smith, *J. Chem. Phys.* **16**, 466 (1948).

² G. H. Twigg, *Proc. Roy. Soc. A* **178**, 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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August 18, 1948

THE analysis of the Raman spectra of substances like tetraethyl orthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ 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 $e=4358\text{\AA}$ and $k=4047\text{\AA}$. The spectrograph was a "Huet" glass prism instrument giving a dispersion of about $20\text{\AA}/\text{mm}$ in the region investigated. The mean error of our measurements is about $\pm 2\text{ cm}^{-1}$ for most lines. Microphotometer records were made, and the weakest diffuse lines were measured on these with errors of about $\pm 10\text{ cm}^{-1}$ for the three lower frequencies.

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

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 $\nu_1(\text{CH}_3)$, $\nu_{11}(\text{CH}_3)$, $\nu_1(\text{CH}_2)$, and $\nu_{11}(\text{CH}_2)$, 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 $\delta_1(\text{CH}_3)$ 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 $\delta_{11}(\text{CH}_3)$ or $\delta(\text{CH}_2)$. 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.