at 5.1°) makes the latter difficult to determine accurately by the method used. The values of the rate constant *k* are more accurate, the intercept being confined to a small region by the proximity of points to the $1/k'$ axis. Although there is little doubt that *K* is larger at lower temperatures, it was not felt that the values were of sufficient accuracy to warrant calculation of the thermodynamic constants of the equilibrium. The activation energy, however, may be estimated from the variation in *k* with temperature to be 30 kcal. In view of the fact that the energy of the carbon-to-carbon bond in glycol is of the order of 60–70 kcal., coördination may be responsible for a lowering in the activation energy of 30 to 40 kcal per mole.

TABLE I

PSEUDO-CONSTANTS (TIME IN SECONDS); CONCENTRATIONS IN M./L.

	0°			5.1°
[Glycol]	$[H^+]$ = 0.008 $k' \times 10^3$	$[H^+]$ = 0.004 $k' \times 10^3$	[Glycol]	$[H^+]$ = 0.008 $k' \times 10^3$
0.192	1.70	1.72	0.192	3.85
.0930	1.61	1.58	.0926	3.57
.0334	1.49	..	.0339	2.97
.0239	1.39	..	.0153	2.24
.0147	1.18	1.20		

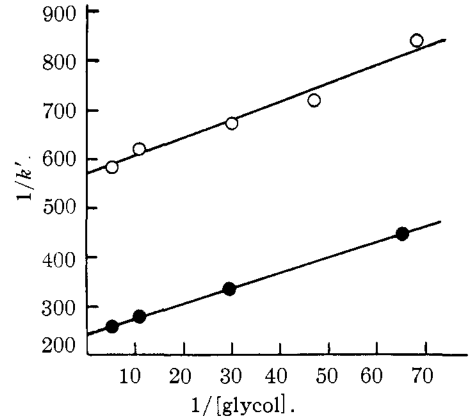

Fig. 1.—Plot of $1/k'$ *vs.* $1/C$: open circles, 0°; solid circles, 5.1°.

Summary

The oxidation of glycol by periodate is shown to proceed through the disproportionation of a coördination compound intermediate involving the oxidizing and reducing agents.

The activation energy is some 30 to 40 kcal. less than one would predict on the basis of the energy necessary to break the carbon-to-carbon bond in glycol; coördination is necessary to the specificity of this type since it is responsible for the lowering of the activation energy.

EAST LANSING, MICHIGAN RECEIVED JUNE 14, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CHICAGO]

Ultraviolet Transmission Limits of Some Liquids and Solids[1a]

BY H. B. KLEVENS[1b] AND J. R. PLATT

In the course of some work on the spectra of solutions in the vacuum ultraviolet,[1,2,3] we have measured the transmission limits of a number of solids and liquids which were being considered for use as windows and solvents in this region. For the liquids, the limits are somewhat related to the position of the first strong absorption band maximum, and so are linked with the values of the first ionization potential. The limits have proved useful as partial criteria of the purity of the solvents.

Except for one small table[1] no previous reports have appeared on solvents suitable for the extreme ultraviolet below 1850 Å., but there have been several reports[4–7] on types of solvents for the quartz ultraviolet. In particular, some recent work has aimed at attaining spectroscopic purity in the quartz region in solvents of the same type as those studied here. Maclean, Jencks and Acree[8] showed that the transmission limits of various saturated hydrocarbons and other solvents could be shifted to shorter wave lengths by the removal of small traces of mercaptans. Stepwise purification of these liquids resulted in final transmission limits near 2000 Å. for the saturated hydrocarbons in a 1-cm. cell. The method of purification used was that described by Mair and White,[9] and Mair

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[1a] Presented before the Division of Physical and Inorganic Chemistry at the 110th meeting of the American Chemical Society at Chicago, Illinois, September 9–13, 1946.

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(1) J. R. Platt, I. Rusoff and H. B. Klevens, *J. Chem. Phys.*, **11**, 535 (1943).

(2) I. Rusoff, J. R. Platt, H. B. Klevens and G. O. Burr, THIS JOURNAL, **67**, 673 (1945).

(3) J. R. Platt and H. B. Klevens, *Revs. Modern Phys.*, **16**, 182 (1944).

(4) A. Castille and V. Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

(5) G. Scheibe and H. Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1934).

(6) F. Twyman and C. B. Allsopp, "Practice of Absorption Spectrophotometry with Hilger Instruments," 2nd ed., Adam Hilger, London, 1934, p. 66.

(7) F. P. Zscheile, J. W. White, Jr., B. W. Beadle and J. R. Roach, *Plant Physiol.*, **17**, 331 (1942).

(8) M. E. Maclean, P. J. Jencks and S. F. Acree, *J. Research Natl Bur. Standards*, **34**, 271 (1945).

(9) B. J. Mair and J. D. White, *ibid.*, **15**, 51 (1935).

and Forziati[10] which involved essentially the use of activated silica gel as an adsorbent. In another study, Graff, O'Connor and Skau[11] used a series of adsorbents such as silica gel, alumina, magnesium oxide, various activated clays and carbons, both in columns and by a slurry procedure, in endeavoring to remove the adsorbing chromophores from several hydrocarbon solvents. Several hydrocarbons were shown to have been purified sufficiently to transmit to about 2300 Å., the limit of the Bausch and Lomb medium quartz spectrograph used in their measurements.

The results in these studies were to be expected, for it had been previously shown[1] that *n*-heptane transmits to about 1700 Å. and isoöctane to 1780 Å., in 0.3-mm. cells when purified in this way.

Apparatus and Procedure

The apparatus is arranged like that of Scheibe[12] with modifications and techniques used previously.[1] The transmission limits given here are the wave lengths of the last visible blackening on a spectrogram for reasonable exposure and development times. For most of the materials described here, the absorption rises suddenly and steeply at the limit. The limits, in consequence, are surprisingly independent of cell thickness, exposure time, personal bias and other variables, the spread in values between runs being no greater than 10 Å. in most cases. A few instances of more gradual approach to the limit will be noted below. The limits given appear to correspond to transmissions of the order of 10 per cent.

Various methods were used to purify the solvents studied. The saturated hydrocarbons were usually shaken repeatedly with concentrated sulfuric acid until the acid layer was no longer colored. These compounds were also passed through a number of silica gel columns, according to the method described by Mair and co-workers.[9,10] Subsequent treatment involved distillation through various Podbielniak columns having the equivalent of either 50 or 100 plates, with a cut-off at a reflux ratio of about 30–40 to 1 (see Tables II, III and IV for further details on individual solvents). Water, acetone, dioxane, alcohols, ether, chloroform and carbon tetrachloride were purified by other appropriate methods (see Table VI).

Transmission Limits

A. Solids.—The limits for the various solids and possible window materials studied are given in Table I. The fused quartz samples appear to be almost as transparent as crystal quartz. A cell with reasonably thick fused quartz windows can then be used for vapor studies at known pressures to 1560 Å. Another promising material is artificial sapphire. The sample here is thicker than that examined by Freed, McMurray, and Rosenbaum[13] and gives a slightly longer wave length limit. Quartz and sapphire are useful for studies on water solutions or corrosive liquids which attack fluorite or lithium fluoride windows. The synthetic fluorite transmits better than lithium fluoride down to at least 1400 Å., which is near the useful limit of our spectrograph. The fluorite windows do not seem to solarize as badly as the lithium fluoride under prolonged exposure, but they show a worse tendency to chip at the edges in handling.

TABLE I

ULTRAVIOLET TRANSMISSION LIMITS OF SOLIDS

Material (source)	Thickness, cm.	Limit, Å.
Lithium fluoride[d]	0.6	Below 1350[a,c]
Fluorite[d]	.6	Below 1350[a]
Fused quartz[e]	.03	30–50% at 1650–1570; 5% at 1550; cut-off 1525
	.4	1600
Fused quartz[f]	.4 (windows on 4 cm. cell)	1560
Crystal quartz	.2	Est. 70% at 1750–1650 Est. 25% at 1550 Est. 20% at 1525 Limit at 1520
Artificial sapphire[g] (Al_2O_3)	.5	1560–1480[b]
Metaphosphate glass[h]	.5	2050
Polyethylene	.01	2800–2270[b]
Spinel[g]	.2	1840
Polyfluoroethylene	.013	2350–1950[b]
	.14	2400–2150[b]
Methyl methacrylate	.20	2600

[a] Limit of spectrograph. [b] Gradual cut off. [c] W. A. Baum, *et al.* (*Phys. Rev.* **70**, 781 (1946)) report a transmission limit of 1100 Å. through a 2-mm diameter sphere of synthetic lithium fluoride. Dr. R. D. Cowan has also obtained the same limit in this Laboratory with a thickness of a few tenths of a mm. [d] Harshaw Chemical Co. [e] Nieder Fused Quartz Co. [f] General Electric Co. [g] Elgin Watch Co. [h] American Optical Co.

The polyethylene and polyfluoroethylene plastics were included in this study to see what effect the complete fluorination of a hydrocarbon would have on the transmission limits. However, the samples tested may be incompletely polymerized or may contain impurities, or the limits may be due to the presence of different plasticizers, since their limits are quite different from those of the completely fluorinated liquids discussed below. The second sample of the polyfluoroethylene seems to have a lower absorption coefficient than the first, if the difference in thickness is taken into account.

B. Liquids.—The transmission limits for the various liquids studied are given in Tables II

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[10] B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards* **32**, 151, 165 (1944).

[11] M. M. Graff, R. T. O'Connor and E. L. Skau, *Ind. Eng. Chem., Anal. Ed.*, **16**, 556 (1944).

[12] G. Scheibe, *Z. physik. Chem.*, **B5**, 355 (1929).

[13] S. Freed, H. L. McMurry and E. J. Rosenbaum, *J. Chem. Phys.*, **7**, 853 (1939).

to VI and Figs. 1 and 2. The data for the C_5, C_6, C_7, C_{10} and C_{12} straight-chain hydrocarbons are summarized in Table II. The limits of these hydrocarbons after purification fall between 1700–1730 Å. The effects of side chains on the transmission limits are tabulated in Table III. Evidently the lowest transmission limits obtained after repeated purification move in general to longer and longer wave lengths as the amount of branching increases. An index of the extent of branching is the maximum number of substitutions around any C–C bond. Within experimental error, the limits of the compounds measured seem to depend solely on this number, as shown by the data in Table III. Some limits previously reported for vapors by other workers[14–16] are included in Table II and enable the data to be extended to the case of zero substitution. This extension is only approximate, as the pressures and cell lengths for the vapors are unfortunately different for the different cases shown. The ethane values would shift to slightly longer wave lengths with increasing cell length or vapor pressure.

TABLE II

TRANSMISSION LIMITS OF STRAIGHT CHAIN SATURATED HYDROCARBONS (0.13 MM. CELL)

Compound (source)	Treatment	Limit, Å.
Ethane	Vapor	1550–1660[a]
n-Pentane[e]	None	2050–1950[b]
	H_2SO_4	1710
n-Hexane[f]	None	2020[c]
	H_2SO_4, SiO_2	1705[c]
	Vapor	1700[d]
n-Heptane[f]	None	1960[c]
	H_2SO_4	1705[c]
n-Heptane[g]	None	1730
	H_2SO_4, SiO_2	1700
	SiO_2, dried over Na	1740
	Catalytic hydrogenation	1705
	Vapor	1700[d]
n-Decane[h]	None	1725
n-Dodecane[h]	None	1730

[a] Ethane vapor, various pressures and cell lengths. See reference 15. [b] Gradual cut-off. [c] See reference 1. [d] See reference 16. [e] Phillips pure grade. [f] Eastman Kodak. [g] Westvaco Chlorine Products Company. [h] National Bureau of Standards.

TABLE III

TRANSMISSION LIMITS OF SATURATED HYDROCARBONS HAVING VARIOUS NUMBERS OF SIDE CHAINS (0.13 mm. CELL)

Compound (source)	Treatment	Limit, Å.	No. subst. around C–C bond
3-Methylhexane[c]	H_2SO_4	1730	3
2,3-Dimethylpentane[c]	H_2SO_4	1770[a]	4
Neohexane	None	2010	4
(2,2-dimethylbutane)	SiO_2	1780[a]	
	H_2SO_4, SiO_2	1760[a]	
Triptane (2,2,3-trimethylbutane)[c]	H_2SO_4	1780[a]	5
Isoöctane	None	1780[a,b]	4
(2,2,4-trimethylpentane)[d]	SiO_2	1780[a,b]	
	H_2SO_4, SiO_2	1780[a,b]	
2,2,3-Trimethylpentane[e]	None	1790	5
2,2,3,3-Tetramethylpentane[e]	None	1795	6

[a] Gradual cut off. [b] See reference 1. [c] General Motors. [d] Rohm and Haas (certified). [e] A.P.I.–N.B.S. These samples of A.P.I.-N.B.S. hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the A.P.I. Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the A.P.I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from materials supplied by the following laboratories:

2,2,3-Trimethylpentane, by General Motors Corporation, Detroit, Michigan, through the operations of the American Petroleum Institute Committee on Hydrocarbons for Spectrometer calibration. (Impurity: 0.32 ± 0.20 mole per cent.)

2,2,3,3-Tetramethylpentane, by the American Petroleum Institute Research Project 45 at the Ohio State University, Columbus, Ohio, under the supervision of C. E. Boord, through the operations of the American Petroleum Institute Committee on Hydrocarbons for Spectrometer Calibration. (Impurity: 0.060 ± 0.020 mole per cent.)

Cyclohexane, by the Barrett Division of the Allied Chemical and Dye Corporation, New York, New York. (Impurity: 0.003 ± 0.002 mole per cent.)

Methylcyclohexane, half by the Barrett Division of the Allied Chemical and Dye Corporation, New York, N. Y., and half by the American Petroleum Institute Research Project 45 at the Ohio State University, Columbus, Ohio, under the supervision of C. E. Boord. (Impurity: 0.10 ± 0.08 mole per cent.)

Cyclopentane, the Tide Water Associated Oil Company, Associated, California, through the operations of the American Petroleum Institute Committee on Hydrocarbons for Spectrometer Calibration. (Impurity: 0.026 ± 0.009 mole per cent.)

Methylcyclopentane, the Houdry Process Corporation, Marcus Hook, Pennsylvania. (Impurity: 0.16 ± 0.06 mole per cent.)

Benzene and toluene, by the A. P. I. Research Project 6 on the "Analysis, purification and properties of hydrocarbons," at the National Bureau of Standards. (Impurity: benzene, 0.06 ± 0.03 mole per cent: toluene, 0.05 ± 0.02 mole per cent.)

It is just possible that this apparent dependence of transmission limit on branching is spurious since the sulfuric acid treatment may have caused rearrangement of the side chains or the formation of degradation products, as discussed by Whitmore.[17] Thus the number of substitutions in Table III may not correctly represent the liquids as finally put into the absorption cell. However, in several cases where the refractive index and boiling point were checked following the acid treatment and fractionation, the correct values were obtained. It is noteworthy that the acid treatment has never

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(14) A. B. F. Duncan and J. P. Howe, *J. Chem. Phys.*, **2**, 851 (1934).

(15) W. C. Price, *Phys. Rev.*, **47**, 444 (1935).

(16) E. P. Carr and H. Stücklen, *Z. physik. Chem.*, **B25**, 57 (1934).

(17) F. C. Whitmore and H. H. Johnson, Jr., THIS JOURNAL, **63**, 1481 (1941)

produced a shift of the transmission limit to *longer* wave lengths.

The effect of ring closure on transmission limits is shown in Table IV. The Eastman Pure grade cyclohexane and methylcyclohexane contained appreciable amounts, of the order of 2 mole per cent., of benzene and toluene, respectively, as determined from their spectra.[18] Further fractionation of this sample of cyclohexane taking a cut at 80.9° (n^{20}D 1.4237) did not result in a further change in the transmission limit. The limit at about 1765 Å. just coincides with the beginning of a group of close bands in the spectrum of cyclohexane vapor as reported by Scheibe and Grieneisen.[5] The shift produced by adding a branch to a ring is seen to be about 25 Å., or about the same as that from adding one branch to a chain.

Table IV

Transmission Limits of Cyclic Saturated Hydrocarbons (0.13 mm. Cell)

Compound (source)	Treatment	Limit, Å.
Cyclopentane[a]	None	1725
Cyclohexane[b]	None	2110[c]
	Pdbk	2130[c]
	SiO_2	2000[c]
	H_2SO_4, SiO_2	1770
Cyclohexane[a]	None	1765
Methylcyclopentane[a]	None	1750[d]
Methylcyclohexane[b]	None	2060[c]
	Pdbk	2060[c]
	SiO_2	1980[c]
	H_2SO_4, SiO_2	1800
Methylcyclohexane[a]	None	1790

[a] A.P.I.-N.B.S. (see footnote [c] to Table III). [b] Eastman Kodak Co. [c] Traces of aromatics present as seen by absorption in region of 2500–2600 Å. [d] About 0.04 mole per cent. of olefin present.

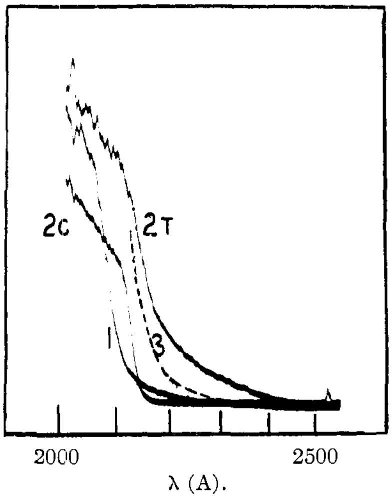

Fig. 1.—Microphotometer tracings of the octenes: (1) octene-1, (2c) octene-2 *cis*, (2t) octene-2 *trans*, (3) octene-1 shifted to red.

Transmission limits of several olefins were studied: octene-1, octene-2 *cis* and octene-2 *trans*. They are not suitable as solvents, but are of interest in showing the effect of unsaturation and the relation between absorption peak positions and limit positions. It can be seen from Table V and from the microphotometer tracing of the spectra of these octenes in Fig. 1, that the octene-1 has a lower transmission limit. The longer wave length limit of the others is due to the double substitution around the C=C bond.[19,20]

Table V

Transmission Limits of Various Unsaturated Hydrocarbons (0.13 mm. Cell)

Compound	B. p., °C.	n^{20}D	Limit, Å.	Peak, Å.	Peak to limit Å.
	Source				
Octene-1[a]	120.5	1.4089	2100	1770	330
Octene-2 *cis*[a]	125.5	1.4146	2130	1830	300
Octene-2 *trans*[a]	124.5	1.4132	2140	1790	350
Propyl nitrile	97.0	1.3664	1800		
Benzene	Eastman Kodak		2700		
	A. P. I.–N. B. S.[b]		2700	1835	865
Toluene	Eastman Kodak		2740		
	A. P. I.–N. B. S.[b]		2740	1885	885

[a] Kindly supplied by Dr. W. Nudenberg. [b] Footnote[c] to Table III.

The octenes-2 also show an easily observable *cis–trans* difference in the way in which the limit is approached as seen in Fig. 1. The spectrograms of the two samples were recorded in immediate succession on the same plate under constant conditions. The octene-2 *cis* transmission breaks sharply at the limit; the octene-2 *trans* begins to absorb several hundred ångströms away.

The absorption coefficients of these octenes have been determined in solution to 1710 Å. and will be reported elsewhere. No trace of dienes was found in these monoölefins as seen from their complete spectra and from the determination of unsaturation by the iodine monochloride method. The approximate wave lengths of the peaks ("N → V transitions") found in these measurements are given in Table V. It is seen that the *trans* peak is at shorter wave lengths than the *cis* peak. Nevertheless, the absorption curves of the two isomers cross over near 2100 Å., as a result of the weak *trans* absorption just mentioned in the 2000–2300 Å. region; so that the *trans* limit given in Table V is at *longer* wave lengths than the *cis*. (Some figures of Carr[21] indicate that pentene-2 *trans* vapor also has stronger average absorption than pentene-2 *cis* vapor in the 2000–2100 Å. region.)

It is thus seen that even for related compounds the wave lengths of the limits may not be perfectly correlated with the wave lengths of the first strong peaks. For non-related compounds,

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(18) J. R. Platt and H. B. Klevens, *Chem. Rev.*, **41**, 301 (1947).

(19) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **4**, 760 (1936); **6**, 55 (1938).

(20) W. C. Price and W. T. Tutte, *Proc. Roy. Soc.* (London), **A174**, 207 (1940).

(21) E. P. Carr and H. Stücklen, This Journal, **59**, 2138 (1937).

TABLE VI

PARAFFIN-TRANSMISSION LIMITS OF VARIOUS NON-PARAFFIN-HYDROCARBON SOLVENTS AND SOLVENT MIXTURES (0.13 MM. CELL)

Compound	B. p., °C.	n_D (°C.)	Limit	Compound	B. p., °C.	n_D (°C.) Source	Limit
Water	Conductivity water		1780[b]	Carbon tetrachloride	76.5	1.4630 (15)	2250–1900[a]
Methyl alcohol	64.6	1.3312 (15)	1890[b]	Diethylamine	54.8	1.3855 (15)	2500
Ethyl alcohol (95%)			1890[b]	Triethylamine	89.5	1.4003 (20)	2600
Ethyl alcohol (absolute)	78.4	1.3624 (19)	1890	Octafluorocyclobutane[e] (C_4F_8)		Dupont	1860 bands[d]
Diethyl ether	34.5	1.3542 (17)	1980[b]				
p-Dioxane	101.5	1.4231 (21)	2030	*n*-Perfluoroheptane (C_7F_{16})		Dupont	1800[c]
Tetrahydrofuran	64.8	1.4075 (21)	2300-2060[a]	*n*-Perfluorononane (C_9F_{20})		Dupont	1830[c]
Acetone	56.5	1.3589 (19)	2000[b]	Ethyl alcohol (absolute)			
				20% in *n*-heptane			1850
Chloroform	61.2	1.4464 (18)	2200[b]	10% in *n*-heptane			1780
				1% in *n*-heptane			1710
				Isoöctane, 10% in *n*-heptane			1730[b]

[a] Gradual cut-off. [b] See ref. 1. [c] In an 0.5 mm. cell. [d] Below 100 cm. pressure. [e] 2 atm. pressure in a 4 cm. cell.

the correlation may be quite poor, as Table V shows, and may be different for different cell lengths, as the curves for water, alcohol and *n*-heptane in Fig. 2 show. It may be worthy of mention that if the octene microphotometer traces of Fig. 1 are displaced so that the three limits coincide, then the octene-1 curve will lie just between the octene-2 *cis* and *trans* curves, as indicated by curve 3. This suggests that the weak 2100 Å. absorption is already present in the octene-1 and is enhanced by the *trans* substitution but suppressed by the *cis*.

The transmission limits of some other unsaturated hydrocarbons are included in Table V. From unreported measurements of other compounds containing double or triple bonds, it has been shown that the first strong absorptions for C=O, C≡C, C=N and C≡N groups occur at shorter wave lengths than the C=C bond peak. The transmission limit of propyl nitrile of 1810 Å. for the 0.13-mm. layer thickness may indicate a maximum below 1600 Å. Included with the unsaturated hydrocarbons are benzene and toluene which show that the transmission limits of solvents are affected even by weak absorptions. As is well known, the limits of these two compounds are not due to the presence of the strong transition in the region of 1850 Å. but are due to the weak forbidden transitions observed in the region of 2600 Å.

The transmission limits of other solvents that are commonly used for spectrophotometric studies are given in Table VI. Included in this table are data for solvent mixtures which have been used by us for studying solutions of organic compounds which were not readily soluble in the straight-chain hydrocarbons. The mixture limits lie at positions intermediate between the limits of the components. The presence of absorbing chromophores in most of these compounds ac-

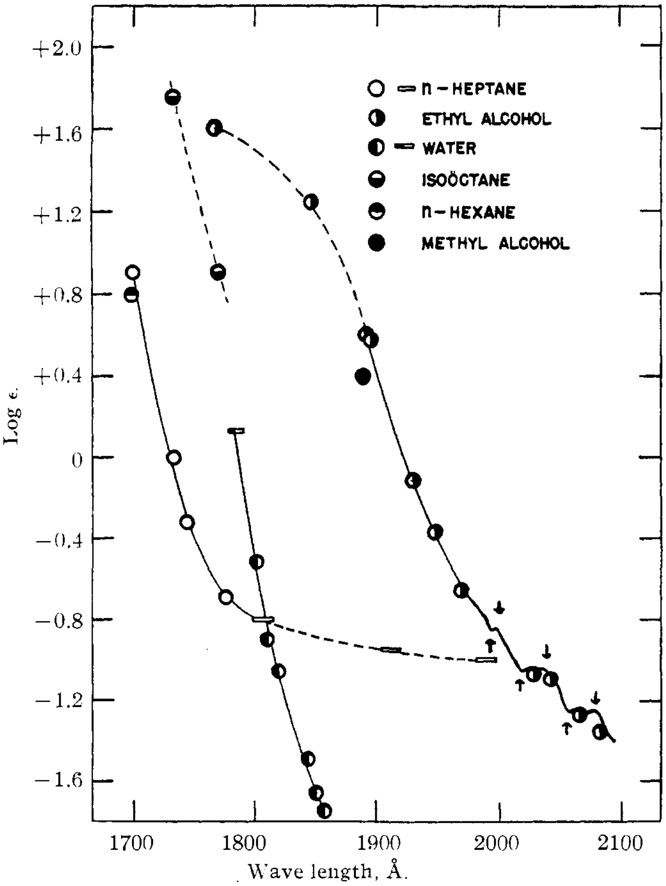


Fig. 2.—Approximate change in molar extinction coefficient of various solvents as determined by variations in layer thickness.

counts for the shift in the transmission limits toward the red and the limits were found to parallel the spectra of these compounds.[22]

Downing, Benning and McHarness[23] reported that many by-products in the preparation of octafluorocyclobutane had refractive indices below 1.30. This suggested the possibility of a very short wave length transmission limit for these compounds. They were kind enough to supply us with samples of liquid *n*-perfluoroheptane (C_7F_{16}) and *n*-perfluorononane (C_9F_{20}). The samples were too small for further purification but were found to transmit to 1800 Å. in 0.50 mm. thickness. They also supplied several grams of very pure octafluorocyclobutane (C_4F_8) vapor which was found to transmit to 1860 Å. at 2 atmospheres pressure in a 4 cm. fused quartz cell. A series of band heads appeared below 1900 Å. at pressures above 100 cm. It is probable therefore that the liquid limits given in Table VI cannot be much reduced by further purification. We hope to examine these bands in the vapor more carefully under higher dispersion.

The data showing the effect of cell thickness on the transmission limit of *n*-heptane, ethyl alcohol and water are given in Table VII. These data are represented by the absorption curves of Fig. 2. These curves are only approximate, possibly subject to uncertainties in ϵ by factors of 2–3, because in making the measurements the geometry of the light path necessarily changes from one cell length to another in arranging the apparatus to exclude air. There is no "perfectly transparent" comparison solvent known for this region with which absolute absorption measurements could be made. The curves confirm the findings of other workers[8] that water is more transparent than *n*-heptane at 2100 Å. The alcohol curve lies lower than those reported by us earlier for primary alcohols,[1] which probably indicates higher purity in the present sample. The bands seen visually at 1980–2100 Å. are at much longer wave lengths than any of those found by Price[24] in the vapor phase. These weak alcohol bands, previously unreported in the case of liquid ethyl alcohol, may account for the fact that alcohol has not been reported as transparent below 2150 Å. Users of quartz spectrophotometers may be able to obtain the lower wave length points on absorption curves in alcohol by using thinner cells.

TABLE VII

EFFECT OF CELL THICKNESS ON TRANSMISSION LIMITS

Cell thickness, mm.	Limits, Å.				
			Ethyl alcohol		
				bands (visual est.)	
	n-Heptane	Water		Max.	Min.
0.135	1700–1705	1785	1890		
.59		1800	1930		
1.08	1735	1810	1950		
2.08	1740–1745	1830	1970		
5.13	1775	1850	2030		
5.76	1800–1830	1855	2045	2000	1980
8.32	1900–1920	1860	2065	2035	2020
10.08	1980–2000	1870	2075	2075	2060

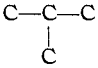
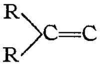
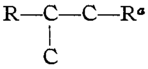
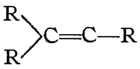
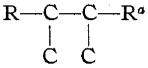
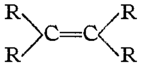
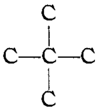
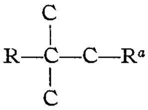
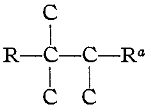
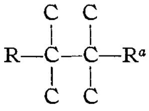
Additional points obtained from solvent mixtures and for *n*-hexane, isoöctane, and methyl alcohol are included in Fig. 2. The difference between the water and alcohol curves is another example of the familiar red shift with alkylation of a chromophore. The difference between the *n*-heptane and the isoöctane curves is an example of the red shift noted above with branching in saturated hydrocarbons.

Discussion

The most interesting relationships found here are those among the saturated hydrocarbons. They can be plausibly interpreted thus. One might suppose that analogous to the ethylenes[19,20] the red shift would depend principally on the number of substitutions around some absorbing center such as a C–C bond and would be almost independent of the length of the alkyl groups substituted (see Table VIII). Secondary shifts of a few ångströms might be produced by the distribu-

TABLE VIII

POSSIBLE ORDER OF RED SHIFT WITH ALKYLATION CONSIDERING C—C AS THE NUCLEUS COMPARED WITH THOSE AROUND C=C

Number of substitutions	Type	Type	Order of red shift for C=C
0–0	C—C	C=C	
1–0	C—C—C	R—C=C	1
1–1	R—C—C—R[a]	R—C=C—R	2b
2–0	 $\mathrm{C{-}\underset{\underset{\textstyle C}{\vert}}{C}{-}C}$	 $\mathrm{\genfrac{}{}{0pt}{}{R}{R}{>}C{=}C}$	2a
2–1	 $\mathrm{R{-}\underset{\underset{\textstyle C}{\vert}}{C}{-}C{-}R}^{a}$	 $\mathrm{\genfrac{}{}{0pt}{}{R}{R}{>}C{=}C{-}R}$	3
2–2	 $\mathrm{R{-}\underset{\underset{\textstyle C}{\vert}}{C}{-}\underset{\underset{\textstyle C}{\vert}}{C}{-}R}^{a}$	 $\mathrm{\genfrac{}{}{0pt}{}{R}{R}{>}C{=}C{<}\genfrac{}{}{0pt}{}{R}{R}}$	4
3–0	 $\mathrm{C{-}\overset{\overset{\textstyle C}{\vert}}{\underset{\underset{\textstyle C}{\vert}}{C}}{-}C}$		
3–1	 $\mathrm{R{-}\overset{\overset{\textstyle C}{\vert}}{\underset{\underset{\textstyle C}{\vert}}{C}}{-}C{-}R}^{a}$		
3–2	 $\mathrm{R{-}\overset{\overset{\textstyle C}{\vert}}{\underset{\underset{\textstyle C}{\vert}}{C}}{-}\underset{\underset{\textstyle C}{\vert}}{C}{-}R}^{a}$		
3–3	 $\mathrm{R{-}\overset{\overset{\textstyle C}{\vert}}{\underset{\underset{\textstyle C}{\vert}}{C}}{-}\overset{\overset{\textstyle C}{\vert}}{\underset{\underset{\textstyle C}{\vert}}{C}}{-}R}^{a}$		

[a] Compounds reported here.

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[22] H. B. Klevens and J. R. Platt, in preparation.

[23] F. B. Downing, A. F. Benning and R. C. McHarness, U. S. Patent 2,384,821, Sept. 18, 1945.

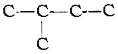
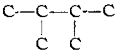
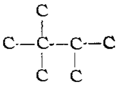
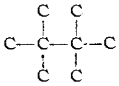
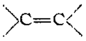
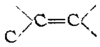
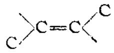
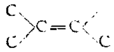
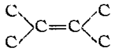
[24] W. C. Price, *J. Chem. Phys.*, **3**, 256 (1935).

tion of the substitutions on the atoms of this bond; just as in the ethylenes the spectrum of butene-2 is only slightly different from that of isobutene. Any C–C bond in the molecule could be thought of as the parent bond but evidently the most substituted bond would have the largest red shift and would therefore determine the transmission limit. The number of bonds which could be counted as having the same maximum substitution would probably make little difference, since the addition of their absorptions would produce negligible shifts in the limit. (Compare the *n*-pentane and *n*-dodecane limits in Table II.)

Taking this view, that the substitutions are to be counted around a C–C bond, would lead to the division of the saturated hydrocarbons from ethane on into the 10 groups shown in Table VIII. Secondary associations would occur between the "1-1" and "2-0" limits (as in the ethylenes), the "2-1" and "3-0", and the "2-2" and "3-1", possibly producing 7 *major* groups. (This compares to the 5 groups, 4 major groups, found in the limits of the ethylenes[19,20] where there are only two positions free for substitution on each carbon.)

TABLE IX

REGION OF THE BEGINNING OF THE FIRST STRONG ABSORPTION

No. subst. around C—C bond	Type	Compound	Beginning of absorption, Å.	Amount of "red shift"
0	—C—C—	Ethane	1550–1600	
1	—C—C—C	Propane		
2	C—C—C—C	*n*-Pentane, etc.	1700–1730	
				~30 Å. ~0.12eV
3	 $\mathrm{C{-}\underset{\overset{\vert}{C}}{C}{-}C{-}C}$	3-Methylhexane, etc.	1730–1740	
				~30 Å. ~0.15eV
4	 $\mathrm{C{-}\underset{\overset{\vert}{C}}{C}{-}\underset{\overset{\vert}{C}}{C}{-}C}$	2,3-Dimethylpentane	1770	
				~15 Å. ~0.06eV
5	 $\mathrm{C{-}\overset{\underset{\vert}{C}}{\underset{\overset{\vert}{C}}{C}}{-}\underset{\overset{\vert}{C}}{C}{-}C}$	2,2,3-Trimethylpentane, etc.	1780–1790	
				~10 Å. ~0.04eV
6	 $\mathrm{C{-}\overset{\underset{\vert}{C}}{\underset{\overset{\vert}{C}}{C}}{-}\overset{\underset{\vert}{C}}{\underset{\overset{\vert}{C}}{C}}{-}C}$	2,2,3,3-Tetramethylpentane	1795	
0		Ethylene	~1730	
				~110 Å. ~0.43eV
1		Propylene	~1840	
				~90 Å. ~0.30eV
2		Butene-2 *trans*	~1930	
				~70 Å. ~0.24eV
3		Trimethylethylene	~2000	
				~40Å. ~0.12eV
4		Tetramethylethylene	~2040	

These predictions seem to fit the observations within the accuracy of measurement. The resemblance between the "red shifts" with alkylation observed for the ethylenes, and those found here for the saturated hydrocarbons is clearly seen in Table IX, where the regions of the beginning of the first strong absorptions are listed.[20] The first two alkylations in both series have the strongest effect; the effects of additional alkylations are seen to be smaller.

These changes parallel roughly those observed in the case of the first ionization potentials. The ionization potential data for the ethylenes were obtained by Price and Tutte[20] from the Rydberg series. These data are presented in Table X which includes also the only available results of electron impact ionization potentials reported for some of the saturated hydrocarbons. The values given are for methane,[25] ethane,[26] propane[27] and *n*- and isobutane[28]; it is probable that more results will soon be available from mass spectrograph and from Schumann studies of hydrocarbon vapors.

TABLE X

IONIZATION POTENTIALS OF SUBSTITUTED ETHYLENES AND METHANES

Ethylene	10.45 eV	Methane	13.1 eV
Propylene	9.6	Ethane	11.6
Butene-2 *trans*	9.2	*n*-Propane	11.3
Trimethylethylene	8.75	*n*-Butane, isobutane	10.3
Tetramethylethylene	8.3	Methylhexane, etc. Triptane, etc.	No available data

In the ethylenes, the changes in the ionization potentials and in the position of the first absorption bands with alkylation have been interpreted in two ways: first, in terms of hyperconjugation; and second, as being due to a simple charge transfer or migration toward the double-bond carbons as a result of the substitution. The latter explanation appears to be the currently accepted one.[29] Presumably it will also be valid for explaining the red shifts in the saturated hydrocarbons discussed here with charge being transferred toward branch carbon atoms.

Further work must be done on the absorption spectra of these paraffins in vapor phase to see whether the shifts observed here in the transmission limits do indeed reproduce with fair accuracy the shifts in the first absorption peaks themselves; and whether Rydberg series can be found which will give more accurate ionization potentials. The propane, *n*- and isobutane and

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(25) L. G. Smith, *Phys. Rev.*, **51**, 263 (1937).

(26) J. A. Hipple, Jr., *ibid.*, **53**, 530 (1938).

(27) J. Delfosse and W. Bleakney, *ibid.*, **56**, 256 (1939).

(28) D. P. Stevenson and J. A. Hipple, THIS JOURNAL, **64**, 1588 (1942).

(29) R. S. Mulliken, *Rev. Modern Phys.*, **14**, 265 (1942).

neopentane transmission limits also need to be measured.

Acknowledgment.—We must again express our appreciation to the University of Michigan for the extended loan of their fluorite spectrograph and to the University of Minnesota for the loan of a hydrogen arc and other equipment. We are indebted to Howard Carter and Dorothy Iker for experimental assistance.

Grateful acknowledgment is made to the American Petroleum Institute and the National Bureau of Standards for the loan of the samples measured in this investigation.

Summary

Limits of vacuum ultraviolet transmission through an 0.13 mm. cell are given for a number of very pure saturated hydrocarbons. The limits depend somewhat on chain length, but more on branching and cyclization. For the non-cyclic paraffins, the limits seem to be determined almost entirely by the maximum number of alkyl substituents on any carbon–carbon bond in the molecule. Limits for some other solvents, for some unsaturated compounds, and for a number of solids are also included. The liquid limits in compounds of a given type are mainly determined by the positions of the first strong absorption band and so are probably closely related to the ionization potentials. The transmission limit of a compound may be used as a partial criterion of purity.

AKRON, OHIO RECEIVED JANUARY 31, 1947

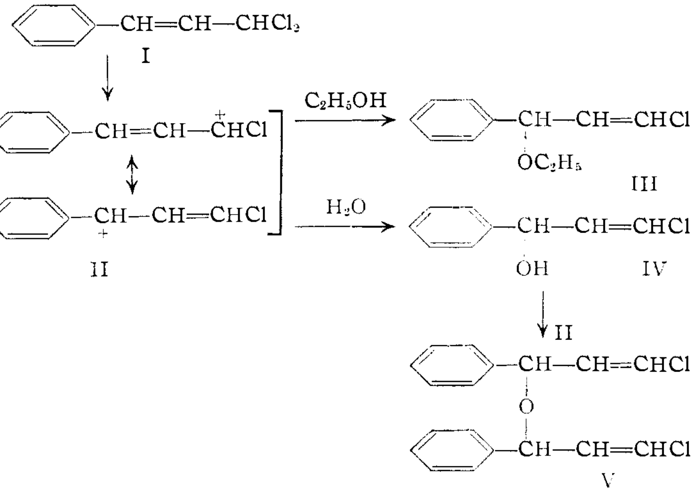
[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Allylidene Halides. III. A Spectrophotometric Study of Solvolysis Reactions of Cinnamal Chloride[1]

BY LAWRENCE J. ANDREWS

In an earlier publication[2] certain observations and proposed mechanisms regarding the hydrolysis and ethanolysis of cinnamal chloride were presented. Although cinnamal chloride has been reported to react with water to yield cinnamaldehyde, it was found that the main product of the reaction at room temperature was bis-(γ-chloro-α-phenylallyl) ether. Only from reactions run under reflux was a considerable quantity of aldehyde isolated. It has also been reported that cinnamal chloride reacts with sodium ethoxide in ethanol solution to form 1-chloro-3-ethoxy-3-phenyl-1-propene.[3] That the reaction also occurred rapidly in absolute ethanol in the absence of sodium ethoxide was confirmed by spectrophotometric procedures.

These and other observations were accounted for on the assumption that cinnamal chloride, a propenylbenzene derivative, undergoes an S_N1 type solvolysis losing chloride ion to form a resonating ionic intermediate which reacts with solvent to form an allylbenzene derivative (see equation 1).

(1)


This paper presents the results of an extension of this work designed to elucidate further the proposed reaction mechanisms. The report that the reaction of cinnamal chloride with sodium ethoxide in absolute ethanol proceeds with complete allylic rearrangement to form 1-chloro-3-ethoxy-3-phenyl-1-propene (III) could be accounted for entirely in terms of the S_N1 type mechanism. In view of a recent observation[4] it seemed important to establish whether or not any of this rearrangement should be ascribed to a bimolecular reaction in which ethoxide ion attacks the dihalide at the double bond adjacent to the phenyl group (equation 2). In addition to a consideration of this question this paper presents further information concerning the factors favoring the production of cinnamaldehyde during the solvolysis of cinnamal chloride.

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(1) Most of the material in this paper was presented before the Organic Division of the American Chemical Society, Atlantic City, New Jersey, April, 1947.

(2) Andrews and Linden, THIS JOURNAL, **69**, 2091 (1947).

(3) Straus and Berkow, *Ann.*, **401**, 121 (1913).

(4) Kepner, Young and Winstein (manuscript submitted for publication) have demonstrated that such a reaction occurs between malonic ester anion and α-methylallyl and α-ethylallyl chlorides.