5% and very probably the figure is lower than this. The small amount of activity present in the sulfite may actually be due to a slight solution of the copper sulfide in the acid that was present or there may be a small amount of reaction between sulfide and sulfite ions. In the case of precipitation of the sulfide in strongly alkaline solution, no reaction between sulfide and sulfite is to be expected but here also a small residual activity seemed to be present in the sulfite carrier, although there was some indication that it might be less than that found in the former case. Normally one would expect the oxidation of sulfur to stop at sulfur dioxide, but as has been already pointed out, the conditions under which the sulfur finds itself in the crystal are far from normal and apparently when oxidation does occur it goes up to the hexavalent state.

The small amount of activity present as sulfite has an additional significance. It means that no appreciable portion of the recoiling sulfur fragments formed in the nuclear reaction Cl^{35} (*n.p.*) S^{35} react chemically with chlorine to form such compounds as SCl_2, S_2Cl_2, etc., for such compounds on hydrolysis give sulfur dioxide. Likewise the absence of sulfite activity indicates the absence of thionates and polythionates.

These various results indicate that the nonsulfate sulfur is either in the form of elementary sulfur or sulfide ions. Attempts to distinguish between sulfur and sulfide ions were unsuccessful because of the rapid exchange that exists between these two states of sulfur in solution.

Heating irradiated potassium chloride crystals above the melting point in an atmosphere of carbon monoxide failed to produce any carbonyl sulfide. This observation would indicate that little or no free sulfur was present, but admittedly this evidence is not too good since under such drastic treatment and in such an unusual habitat free sulfur if present may well undergo some chemical transformation.

Acknowledgment.—The author wishes to express his appreciation to Professor R. D. Fowler for many illuminating discussions which were extremely helpful during the course of this investigation. It is also desired to acknowledge the coöperation of various members of the staff of the Brookhaven National Laboratory where the initial phase of this work was carried out.

Summary

The state of oxidation of S^{35} formed by neutron irradiation of potassium chloride depends on the pre-irradiation treatment of the crystals. If the crystals were carefully outgassed by heating and pumping the radioactive sulfur appeared in part either as sulfur or more probably as sulfide ion. If no precaution was taken to remove air from the crystals all of the S^{35} appeared in the hexavalent state. In all cases tested there was always some activity present as hexavalent sulfur and in the most favorable situation as little as 15% of the total sulfur activity was present in the highest oxidation state. It is concluded that atmospheric oxygen which is occluded in the crystal is responsible for the hexavalent state of the radio sulfur.

BALTIMORE, MARYLAND RECEIVED MAY 5, 1949

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND BROOKHAVEN NATIONAL LABORATORY]

Infrared Spectra of Ortho-, Meta-, Para- and Omega-Monodeuterotoluenes in the 2–16 Micron Region[1a]

BY JOHN TURKEVICH,[1] HUGH A. MCKENZIE,[2] LEWIS FRIEDMAN AND ROBERT SPURR[3]

In connection with studies being carried out on the mechanism of exchange reaction between deuterium and aromatic compounds, it was found necessary to investigate the infrared spectrum of the monodeuterotoluenes. The present paper contains information on the preparation of these compounds and the infrared spectrum in the 2–16 micron region.

Preparation of the Compounds

The various monodeuterotoluenes were prepared by deuterolysis of the appropriate Grignard reagent. The latter was made using the procedure and apparatus of Weldon and Wilson.[4] After the formation of the ether solution of the Grignard reagent, it was connected to a vacuum system and most of the ether was distilled off. It was found preferable not to remove the ether completely since complete removal would make it extremely difficult to effect the reaction between the Grignard compound and the heavy water. The reaction flask was cooled in a Dry Ice–acetone-bath and the heavy water was added dropwise. The system was then allowed to warm up slowly overnight. The reaction mixture was shaken vigorously and then allowed to stand for at least twenty-four hours. The hydrocarbon and remaining ether were removed from the flask

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(1a) Research carried out, in part, under the auspices of the Atomic Energy Commission.

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(4) L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, 235 (1946).

by vacuum distillation to a trap cooled with liquid air. The contents of the trap were then redistilled to obtain a deuterotoluene fraction. The latter was redistilled to obtain a fraction boiling at 110°. The compounds were prepared and purified at the Frick Chemical Laboratory of Princeton University. The mass spectra of all the deutero compounds were examined by Dr. F. Mohler of the National Bureau of Standards. The results indicate that there is less than 0.2% of the dideuterium compound present in each sample and at most 5% of non-deuterated toluene. Further data on the purity will be relegated to the end of the paper.

Materials

o-**Toluidine** was purified by crystallization of the oxalate[5] and the fraction boiling at 182° in a 70-cm. column was collected.

o-**Bromotoluene** was prepared from the *o*-toluidine by the method of Bigelow.[6]

m-**Bromotoluene** was the Eastman Kodak Co. product. Examination of its infrared spectrum showed that it was free from the ortho, para or omega compound.

p-**Toluidine** was purified by crystallization of the hydrochloride.

p-**Bromotoluene** was obtained by diazotization of *p*-toluidine at 5–10°.[7] The product obtained boiled at 183°.

Benzyl chloride was the 181° fraction of the Paragon benzyl chloride.

Toluene was a special sample obtained from the U. S. Bureau of Standards.

Heavy water of 99.8% purity was obtained from the Atomic Energy Commission.

Results

The infrared spectra in the 2- to 16-micron region were obtained in 0.1-mm. thick rock salt cells on the Baird Associates Double Beam Recording Spectrophotometer[8] of the Chemistry Department of the Brookhaven National Laboratory. The results obtained for toluene, ortho-, meta-, para- and omega-monodeuterotoluene are presented in Table I and Figs. 1–5. The figures contain the absorption both of the pure compound and of a 10% solution in carbon tetrachloride. The data in the carbon tetrachloride solution are of doubtful value in regions of strong absorption of carbon tetrachloride, namely, 705–840 cm.$^{-1}$.

Table I

Absorption Bands of Various Toluenes

Toluene		Deuterotoluenes			
Present work	API 308	Ortho	Meta	Para	Omega
	3040	3040 S			3049 S
3000 VS[a]		2985 S	3010 S	2994 S	3000 S
				2959 S	2960 Sh
2915 VS	2924	2900 S	2907 S	2898 S	2890 S
	2874		2850 S		
2830 M		2830 S		2833 S	2830 S
					2790 M
2740 W	2740	2712 W	2732 W	2717 W	
					2670 W
2600 W	2590	2570 VW	2580 VW	2580 VW	
					2551 W
2535 W	2538				
2520					
	2410		2469 VW		
2380	2364				
2340 W	2336				
2300 W	2315	2315 W	2320 W		
	2283				
2230 VW	2263	2220 M	2252 M	2252 WM	2250 Sh
	2208			2230 M	2210 Sh
2180 VW	2188	2174 VW	2170 VW		
2150 VW	2164	2150 VW			2150 S
	2066		2060 W		
1985 Sh	1988				
1935 M	1941	1930 WM	1931 MW		1923 S
		1908 WM		1894 MW	
		1875 W	1875 WM		
1852 M	1855	1842 W	1855 WM	1845 W	1845 M
1795 M	1802	1800 WM	1900 M		1802 M
				1789 WM	1786 S
1739 M	1736	1718 W	1721 WM	1735 W	1724 W
	1698		1705 W		
1675 WM	1675				
1660 VW		1645 M		1675 WM	
1616 S	1605	1608 S	1616 S	1680 S	1613 S
1587 Sh	1575	1590 W			1565 M
	1527				
1497 S	1497	1504 Sh	1500 Sh	1510 W	
		1481 S	1486 S	1497 S	1499 S
1466 S	1460	1475 Sh	1475 Sh		
		1464 Sh	1462 S	1454 S	1458 S
			1420 W	1420 W	1440 W
1390 S	1379	1380 S	1386 S	1380 S	1386 MS
1339 W	1333		1350 W	1351 WM	1351 M
1316 WM	1314			1310 W	
	1282	1284 W	1295 WM		1285 S
					1277 S
1250 W	1250		1250 VW		
1217 WM	1211	1210 W	1209 WM	1206 W	1210 W
1181 M	1179	1176 WM	1170 M	1179 M	1180 M
1161 W	1156	1156 WM		1151 M	1150 M
		1126 M	1126 M	1126 M	1126 S
				1121 M	
1111 WM	1107	1110 W	1106 S	1111 S	
		1095 W			
1087 S		1085 WM	1085 S	1080 S	1080 S
1082 Sh	1081	1076 W	1076 W	1076 Sh	
1044 S	1042	1045 S	1050 S	1040 S	1045 W
1036 S	1030	1033 Sh		1029 S	1033 S
1005	1003			1013	
	982	985 WB	983 WB	983 W	987 M
	966				
		943 WM		944	
930	930				
		914 W	917 S	917 W	915 M
898 M	896	893 W	894 S	893 W	900 M
878 W	872	865 M	879 MS	863 M	
846 W	844	834 W	836 M	836 S	842 M
		798 WM	800 BS	803 M	807 M
788 WM	786	785} BS		785 M	
		765	763 WM		
730 S	728	725 S	725 S	726 S	
		716 S		710 S	715 S
695 S	694	695 S	695 S	693 S	694 S

[a] *Notation on intensity:* S, strong; M, medium; W, weak; VW, very weak; B, broad; Sh, shoulder.

Data are also given on the spectrum of toluene obtained by the Naval Research Laboratory and published by the American Petroleum Institute under the serial number 308.

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(5) L. Vanino, "Handbuch der präparativen Chemie," Vol. 2, Ferd. Enke, Stuttgart, 1914, p. 438.

(6) Bigelow in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 130.

(7) Bigelow, *ibid.*, p. 183.

(8) W. S. Baird, H. M. O'Bryan, C. Ogden and D. Lee, *J. Opt. Soc. Amer.*, **37**, 754 (1947).

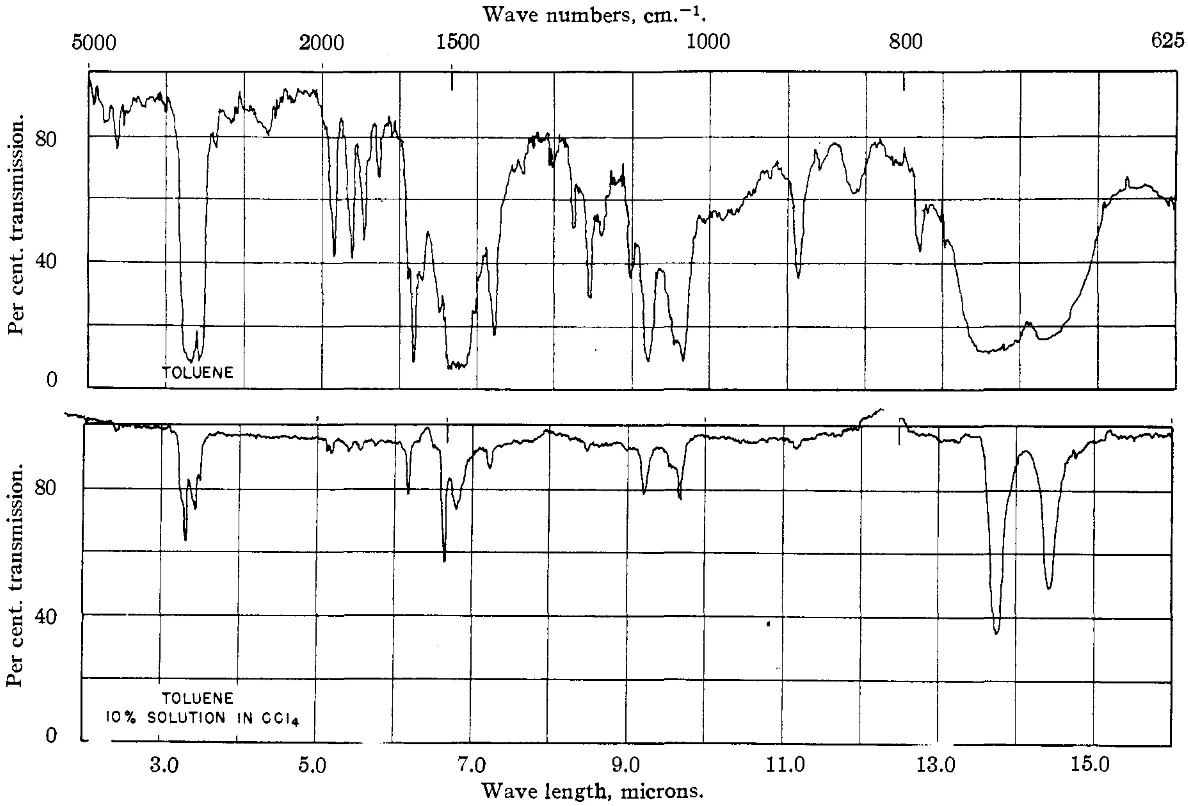

Fig. 1.—Infrared spectrum of toluene.

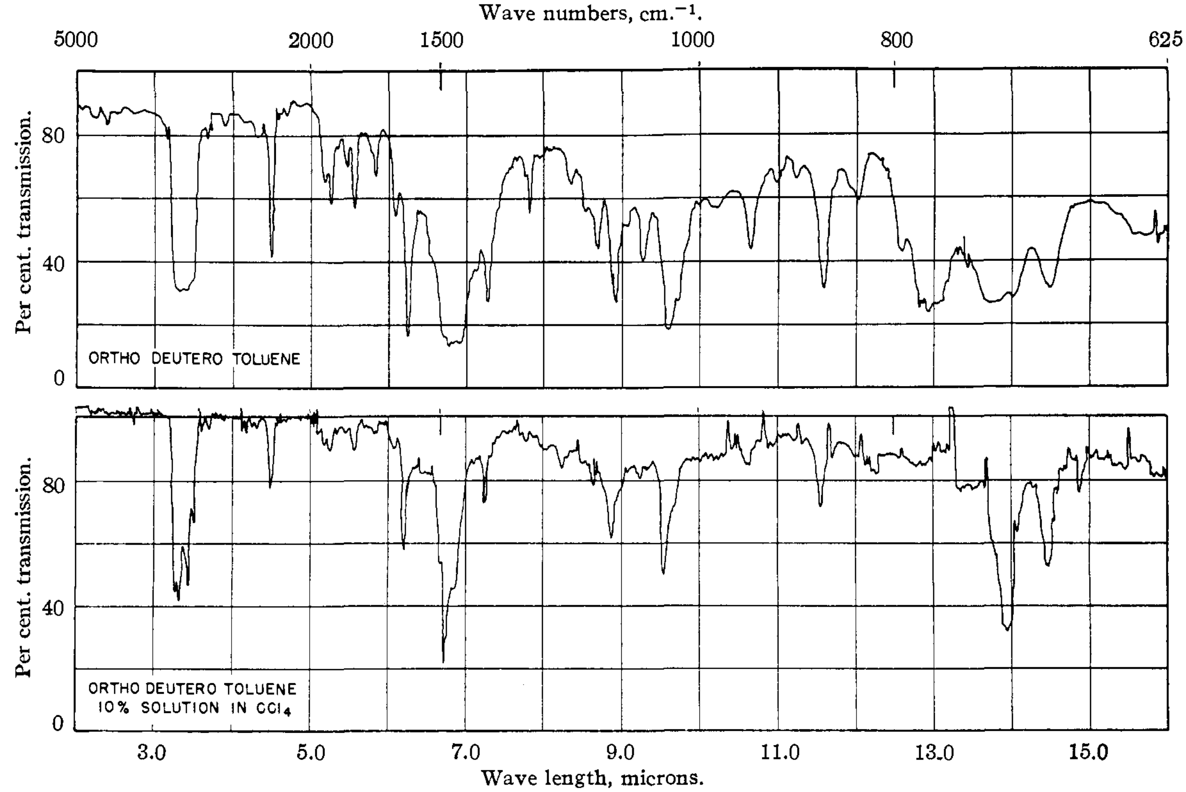

Fig. 2.—Infrared spectrum of *o*-deuterotoluene.

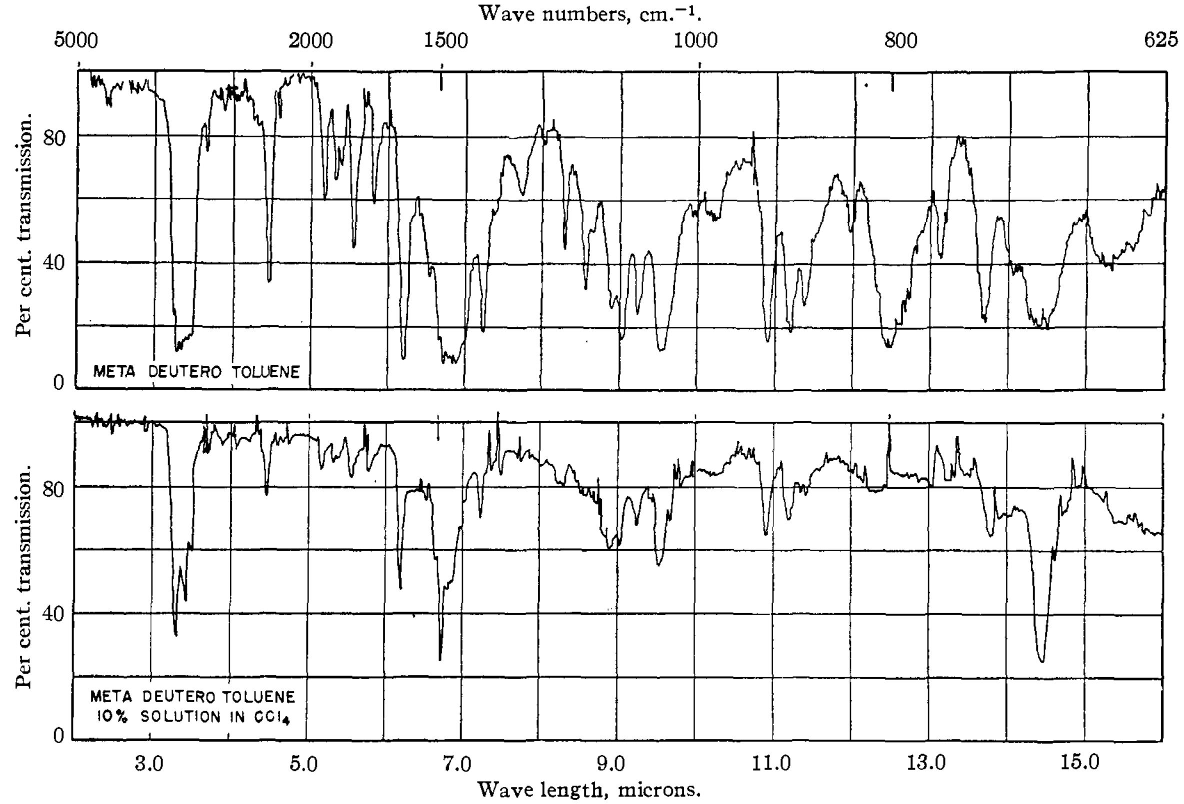

Fig. 3.—Infrared spectrum of *m*-deuterotoluene.

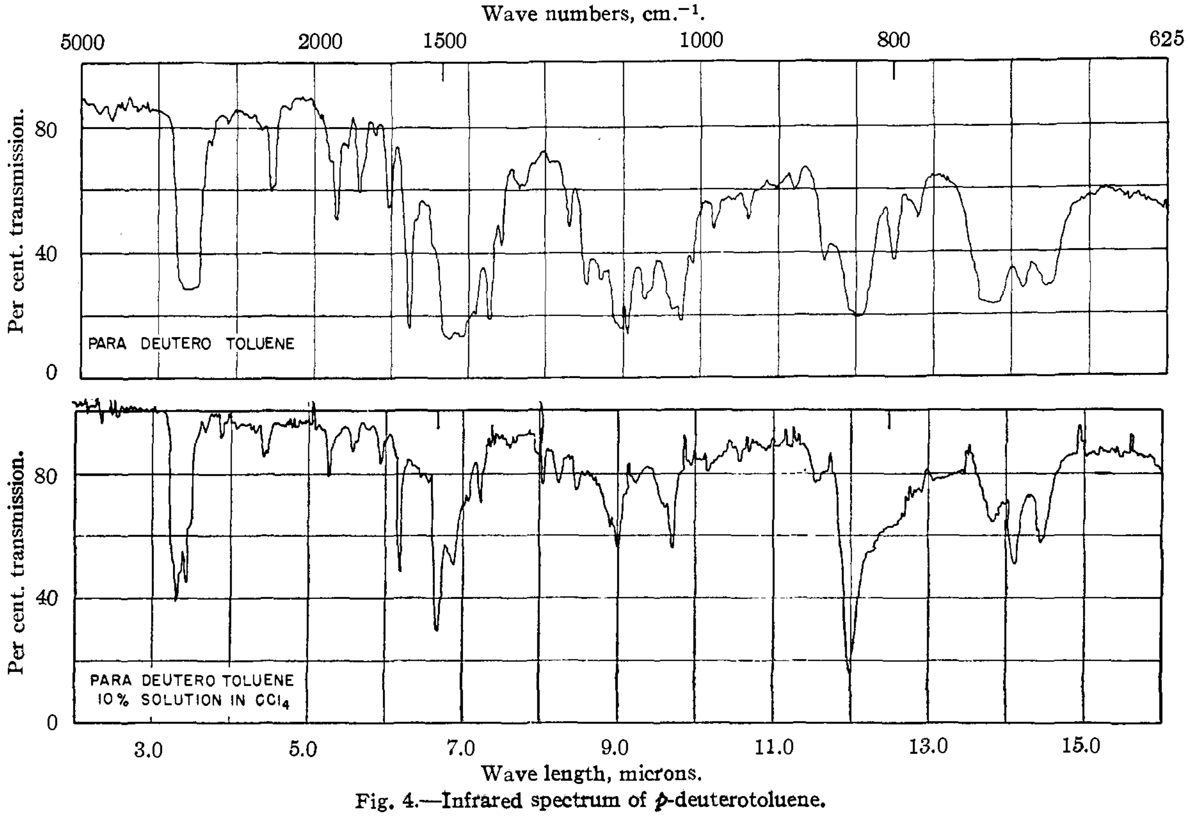

Fig. 4.—Infrared spectrum of *p*-deuterotoluene.

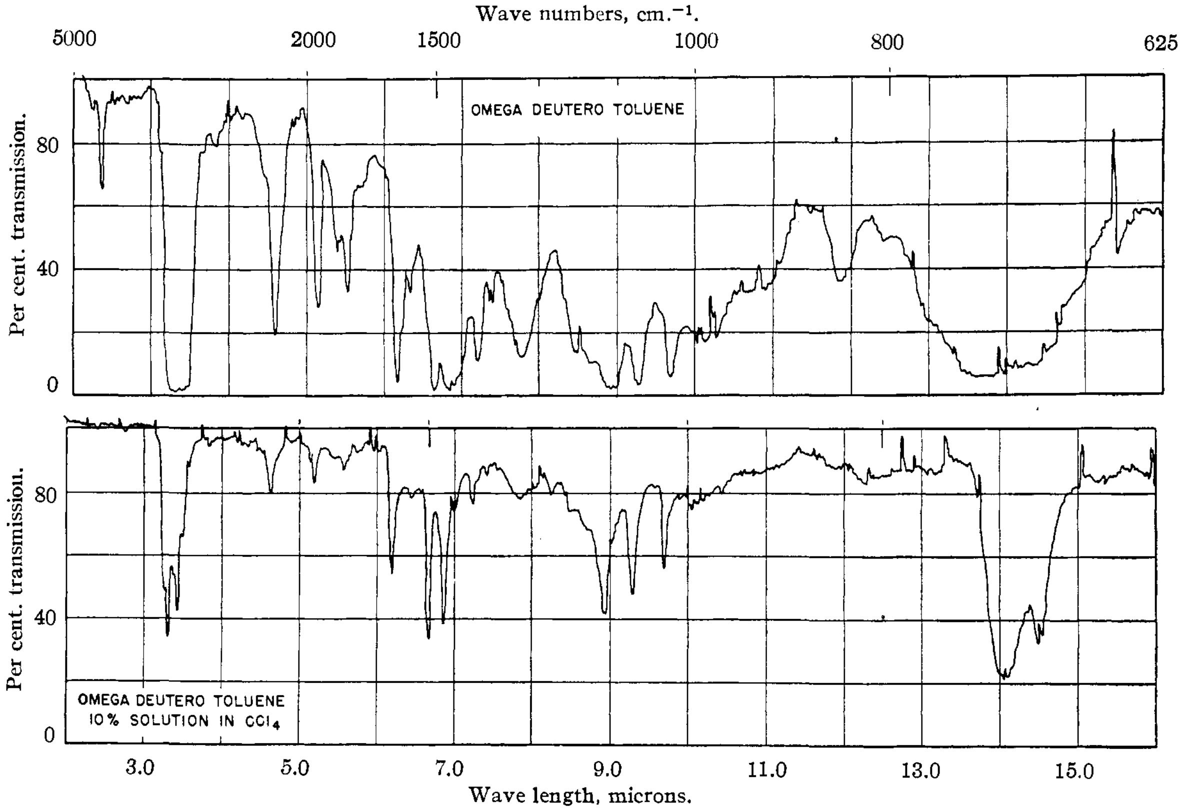

Fig. 5.—Infrared spectrum of ω-deuterotoluene.

Discussion

A complete discussion and interpretation of the results will be withheld until work is completed on spectra in the near infrared at high resolution using lithium fluoride optics, on the spectra in the 16- to 38-micron region using KBr and KRS 5 (thallium bromide–iodide) optics and on the Raman spectra. In the meantime, we wish to record the following observations.

The 4.6-micron region contains the bands due to the carbon–deuterium valence vibration. Non-deuterated toluene shows a very weak absorption in this region, undoubtedly due to an overtone or combination. When the deuterium atom is substituted in the ring the absorption band is at 2220–2252 cm.$^{-1}$, while when the deuterium atom is in the side chain the absorption is at 2150 cm.$^{-1}$. Thus it is easy to distinguish compounds containing deuterium in the ring from those containing deuterium in the side chain. Furthermore, the ortho-monodeutero compound absorbs at 2220 cm.$^{-1}$, the meta- at 2252 cm.$^{-1}$, and in the para compound the band is split in two at 2230 and 2252 cm.$^{-1}$. The per cent. of transmission of this carbon–deuterium stretching frequency is less in the meta compound than in the ortho compound and is least in the double peak of the para compound. All these bands are relatively sharp while that in the omega compound is rather broad and of the same intensity as that of the meta compound.

We would also like to discuss the purity of the compounds on the basis of the infrared data obtained. It is not possible to find a band that is characteristic of the non-deuterated toluene in this region of the infrared spectrum. The band at 730 cm.$^{-1}$ would satisfy this criterion were it not for the fact that the para compound has a broad band at 726 cm.$^{-1}$. The omega compound can be identified easily by the position of its carbon–deuterium stretching band at 2150 cm.$^{-1}$. The weakness of the absorption of other compounds in this region indicates the absence of the side-chain substituted deuterium in the ring-substituted deuterium compounds. The band at 1645 cm.$^{-1}$ can be used to establish the absence of the ortho compound in the meta, para and omega samples. The band at 879 cm.$^{-1}$ in the meta compound can be used to indicate the absence of this compound in the ortho, para and omega samples. The band at 1675 cm.$^{-1}$ is present in the para but not in the ortho, meta or omega samples. Thus the purity of the compounds is indicated within the accuracy of the infrared spectrometer.

Summary

The preparation of the ortho, meta, para and omega deuterotoluenes has been described and their infrared spectra from 2 to 16 microns presented.

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