[A CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Reactions of Methyl Radicals with s-Butyl Chloride[1]

BY A. S. KENYON

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The photolysis of acetone has been used as a source of methyl radicals and their subsequent reactions with *s*-butyl chloride have been determined. Hydrogen chloride is not a primary photochemical product. It results from secondary reactions involving the radicals produced by the abstraction of hydrogen atoms from the *s*-butyl chloride and acetone. The compounds producing the hydrogen chloride have been found to be 4-chloro-4-methylhexanone-2 and 3,4-dichloro-3,4-dimethylhexane. The extent of the methyl radical reactions has been determined by the use of deuterated acetone. Quantum yields for the hydrogen chloride production from *s*-butyl chloride have been found to be thermally dependent. The quantum yield at 25° is 0.08 while at temperatures above 100° the yield approaches unity. The quantum yield is temperature dependent even at temperatures where the quantum yield for the production of carbon monoxide from the photolysis of acetone remains constant.

Introduction

During the course of investigations on the photodegradation of polyvinyl chloride carried out in this Laboratory, the free radical reactions of secondary butyl chloride were studied. Considerable work has been reported by Steacie and co-workers[2] on the reactions of methyl radicals upon various types of compounds. The present study involves the reactions of methyl radicals produced from the photolysis of acetone upon *s*-butyl chloride.

Experimental

The *s*-butyl chloride (Eastman Kodak Co. white label) was purified by washing with alkaline permanganate, water, dried over $CaSO_4$ and fractionally distilled in a 100-plate helices-packed column. The center fraction boiling at 68° was used for all experiments.

The acetone was dried over $CaSO_4$ and distilled in a 100-plate column, the middle third being retained.

The apparatus for irradiating and sampling the *s*-butyl chloride and acetone mixture was of conventional design consisting of a gas reaction cell with Corex D windows, liquid trap, circulating pump and Toepler pump. The reaction cell was heated electrically to the desired temperature. The radiation was produced by a General Electric AH-6 mercury lamp with a suitable optical system. Light of wave length 3130 Å. was isolated by a filter system described by Noyes and Leighton.[3] The absorbed energy of this wave length within the reaction cell was of the order of 1×10^{16} quanta per second as measured by the liberated carbon monoxide.

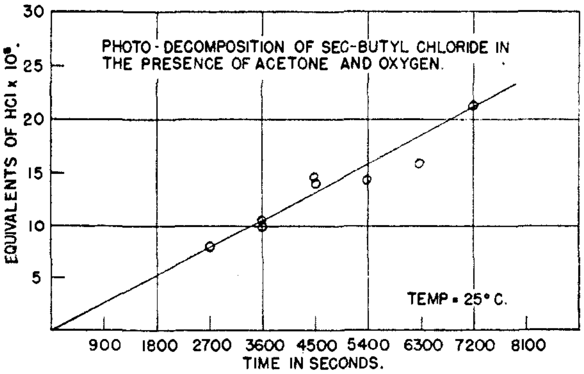

Fig. 1.—Photo-decomposition of *s*-butyl chloride in the presence of acetone and oxygen.

After the desired irradiation, the products were separated by collecting the condensable vapors in a liquid nitrogen trap and pumping off the non-condensable gases, methane and carbon monoxide, which were analyzed by means of a Westinghouse Mass Spectrometer. The quantity of carbon monoxide produced served as an internal actinometer. The condensable products in the trap were allowed to expand into a volume of 3400 cc. Aliquot samples were analyzed for hydrogen chloride by precipitating the chloride as the silver salt and determining the turbidity of the suspension.

The quantity of hydrogen chloride produced by the photoreaction of *s*-butyl chloride and acetone as a function of time was studied both in the presence and absence of oxygen. A slightly modified gas system was used for these experiments which permitted the addition of known pressures of the vapors. In these experiments 98 mm. of *s*-butyl chloride and 16 mm. of acetone were used. When oxygen was present, 600 mm. was added to the mixture. The reaction cell had a volume of 130 cc. No filter was used and the beam intensity was approximately 5×10^{17} quanta per second ($\lambda > 2700$ Å.) as measured by an uranyl oxalate actinometer.

The deuterated acetone was prepared by a modified method of Halford, Anderson and Bates.[4] The catalyst was NaOD made by dropping a small pellet of sodium metal into 99.8% deuterium oxide (Stuart Oxygen Co.). The deuterated acetone was analyzed by the mass spectrometer and the quantities of D-6, D-5 and D-4 determined. Suitable corrections were applied to the calculations to account for the various degrees of deuteration.

The mercury dimethyl was prepared by the method of Marvel and Gould.[5]

Results

Pure *s*-butyl chloride does not absorb light of wave lengths greater than 2700 Å. If an absorbing material such as a ketone is present, then decomposition of *s*-butyl chloride will take place with evolution of hydrogen chloride.

Figure 1 shows the amount of hydrogen chloride produced with time at 25° when oxygen is present. The quantity of

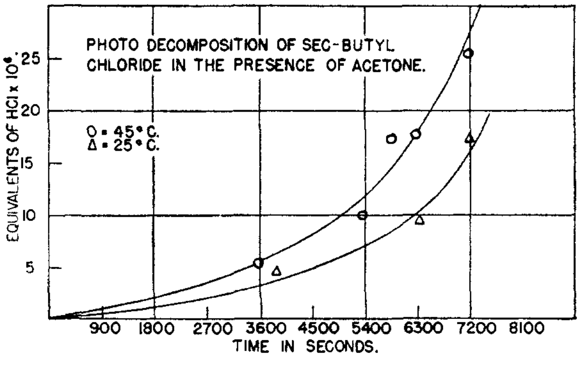

Fig. 2.—Photo-decomposition of *s*-butyl chloride in the presence of acetone.

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(1) Presented in part before the Division of High Polymer Chemistry at the April, 1951, Meeting of the American Chemical Society, Boston, Mass., and before the National Bureau of Standards Symposium on Polymer Degradation, Sept., 1951.

(2) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950); *ibid.*, **19**, 169 (1951).

(3) W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 69.

(4) J. O. Halford, L. C. Anderson and J. Bates, THIS JOURNAL, **56**, 491 (1934).

(5) C. S. Marvel and V. L. Gould, *ibid.*, **44**, 153 (1922).

hydrogen chloride produced is directly proportional to time and the extrapolated curve passes through the origin indicating little or no induction period.

Figure 2 shows the equivalents of hydrogen chloride produced in the absence of oxygen as a function of time at 25 and 45°. There is an acceleration in the amount of hydrogen chloride liberated when *s*-butyl chloride and acetone is irradiated in the absence of oxygen. Initially the rate of hydrogen chloride formation is slower in the absence of oxygen but eventually it exceeds the rate in the presence of oxygen.

The amount of liberated hydrogen chloride in the photodegradation of *s*-butyl chloride is proportional to the concentration of the absorbing substance which in this case is acetone. The equivalents of hydrogen chloride produced by 96 mm. of *s*-butyl chloride when irradiated for 1.5 hours at a temperature of 45° in the presence of varying amounts of acetone from 8 to 30 mm. are shown in Fig. 3.

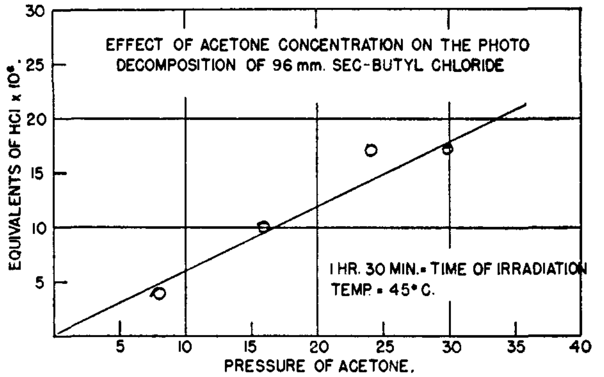

Fig. 3.—Effect of acetone concentration on the photodecomposition of 96 mm. of *s*-butvl chloride.

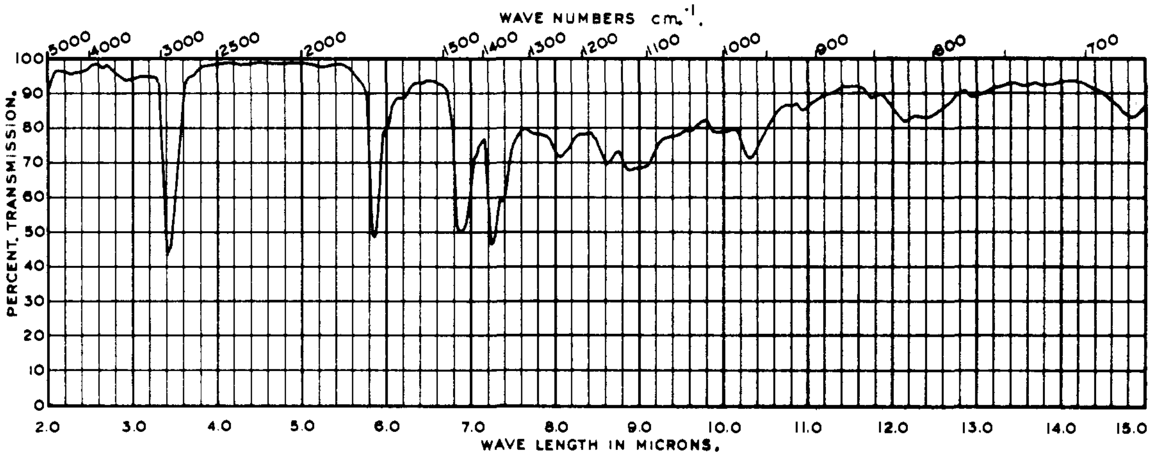

Fig. 4.—Infrared spectrum of high boiling fraction formed during photolysis of acetone in the presence of *s*-butyl chloride at 122°.

The effect of temperature on the quantity of hydrogen chloride liberated has been determined at 25, 45 and 122°.

THE AMOUNTS OF HYDROGEN CHLORIDE PRODUCED IN 1.5 HOURS OF IRRADIATION

Temperature, °C.	Equivalents of HCl × 10⁶
25	7
45	10
122	55

These data do not form a straight line when plotted as an Arrhenius plot. The deviation from a straight line may be caused by the increased concentration of methyl radicals at 122° since many investigators[6] have shown that the quantum yield for carbon monoxide from the photolysis of acetone at temperatures in excess of 100° is unity and that the primary reaction at these temperatures is

$$CH_3COCH_3 + h\nu \longrightarrow 2CH_3\cdot + CO$$

When *s*-butyl chloride and acetone are irradiated by light of wave length of 3130 Å., there are formed carbon monoxide, methane, hydrogen chloride and a high boiling liquid mixture which showed masses at 55, 95, 97, 110, 112 and up to 148, the limit of detection, on the mass spectrometer. The infrared spectrum of this high boiling liquid (Fig. 4) showed the presence of a carbonyl group and the chemical analysis showed 22.24% chlorine by weight. Ethane is formed in a large amount when acetone is irradiated alone, but in the presence of *s*-butyl chloride little or no ethane is formed. Steacie and co-workers[2] have found that the formation of ethane is suppressed in reactions of methyl radicals with hydrocarbons which prevent combination to form ethane.

Mercury dimethyl and *s*-butyl chloride were thermally decomposed at 300° to determine what products were formed by the action of methyl radicals alone upon *s*-butyl chloride. The products of this degradation were identified by the mass spectrometer to be methane, hydrogen chloride and a liquid which showed strong masses of 55, 95 and 110. If *s*-butyl chloride is heated alone at 300°, the products of the reaction are hydrogen chloride and butene-2.

Deuterated acetone was used as a source of free methyl radicals to determine the extent of the reaction by measuring the CD_4 and CD_3H ratios.

When the vapor composition in the reaction cell consisted of 36 mm. of *s*-butyl chloride and 157 mm. of acetone containing deuterated acetone as a tracer at a temperature of 122°, 11.1% of the methyl radicals produced by the photolysis of acetone react with the acetone to form methane and acetonyl radicals while 88.9% of the methyl radicals attack the *s*-butyl chloride to produce methane and *s*-butyl chloride radicals.

The following quantum yields were determined for hydrogen chloride and methane at a wave length of 3130 Å. and at 122°:

Φ_{HCl}	1.04	1.29	1.00	1.02	1.09 ± 0.11
Φ_{CH_4}	2.12	2.20	2.00	2.00	2.08 ± 0.09
Φ_{CO}	1	1	1	1	1

After the reaction, the tube containing the condensed liquids was warmed to approximately 150° to hasten the distillation into the expansion chamber. If the liquid in the trap is allowed to expand without heating then the quantum yield for HCl drops to 0.8 instead of unity for the reaction at 122°.

If the photodecomposition of *s*-butyl chloride and acetone is carried out at 25°, the quantum yield for HCl is approximately 0.07 and the quantum yield for methane is 0.08. Under these conditions, the primary reaction for the photolysis of acetone is

$$CH_3COCH_3 + h\nu \longrightarrow CH_3\cdot + CH_3\dot{C}O$$

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[6] W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948); W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947).

and the quantum yield for the production of CO is approximately 0.1.

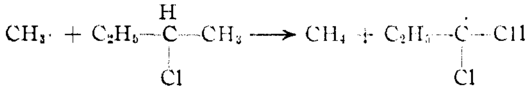
Discussion

Since the only substance which can absorb light of wave length 3130 Å. is acetone, the primary reaction must be the decomposition of the ketone.

$$CH_3COCH_3 + h\nu \xrightarrow{122°} 2CH_3\cdot + CO \quad (1)$$

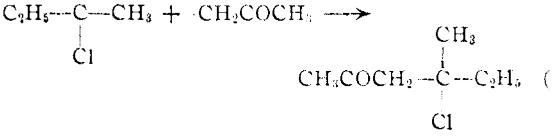
$$CH_3\cdot + CH_3COCH_3 \longrightarrow CH_4 + .CH_2COCH_3 \quad (2)$$

It has been shown by the use of deuterated acetone that some of the methane is produced by the abstraction of a hydrogen atom from the *s*-butyl chloride as shown in reaction (3).



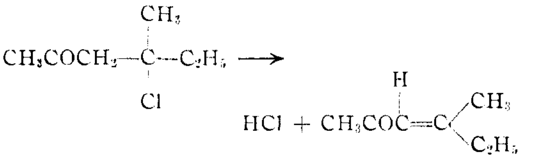
$$CH_3\cdot + C_2H_5-\overset{H}{\underset{Cl}{C}}-CH_3 \longrightarrow CH_4 + C_2H_5-\underset{Cl}{\dot{C}}-CH_3 \quad (3)$$

No acetonyl acetone was observed in the mass spectra of any of the products. The infrared spectrum of the liquid product showed the presence of a carbonyl group at 5.8 microns which could arise from the combination of an acetonyl radical with the *s*-butyl chloride radical as shown in the reaction



$$C_2H_5-\underset{Cl}{\dot{C}}-CH_3 + \cdot CH_2COCH_3 \longrightarrow CH_3COCH_2-\overset{CH_3}{\underset{Cl}{C}}-C_2H_5 \quad (4)$$

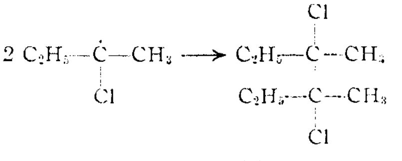
forming 4-chloro-4-methylhexanone-2. This ketone is unstable and would readily dehydrohalogenate to form the unsaturated ketone, 4-methylhexene-3-one-2, as



$$CH_3COCH_2-\overset{CH_3}{\underset{Cl}{C}}-C_2H_5 \longrightarrow HCl + CH_3CO\overset{H}{C}=C\begin{matrix}\diagup CH_3\\ \diagdown C_2H_5\end{matrix} \quad (5)$$

If the acetonyl radicals had reacted with the *s*-butyl chloride to form *s*-butyl chloride radicals by removing the hydrogen atom on the tertiary carbon, no ketone other than acetone would be produced and no high ketone would have been found in the high boiling liquid residue (b.p. approx. 170°). The methyl radicals are responsible for the production of the *s*-butyl chloride radicals in these reactions.

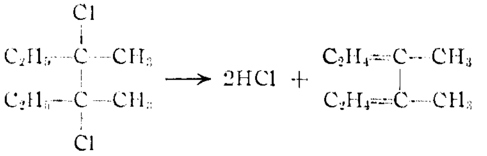
The photolysis of deuterated acetone in the presence of *s*-butyl chloride produced a greater amount of *s*-butyl radicals than acetonyl radicals (88.9 to 11.1%). The *s*-butyl chloride radicals may react with an equivalent amount of acetonyl radicals and the excess of butyl chloride radicals dimerize as shown in the reaction



$$2\ C_2H_5-\underset{Cl}{\dot{C}}-CH_3 \longrightarrow \begin{matrix} C_2H_5-\overset{Cl}{C}-CH_3 \\ | \\ C_2H_5-\underset{Cl}{C}-CH_3 \end{matrix} \quad (6)$$

The resulting mixture of *β*-chloro ketone and 3,4-dichloro-3,4-dimethylhexane contains 22.2 mole per cent. of the ketone and 77.8 mole per cent. of the dimer. Such a mixture would contain 36.0% by weight chloride. The chemical analysis for chlorine on the high boiling liquid and evolved hydrogen chloride using normal acetone showed 36.6% by weight.

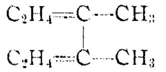
The mass spectrum of the high boiling liquid showing mass units at 55, 95, 97, 110 and 112 indicates the presence of two or more compounds in this liquid since no possible combination of atoms containing oxygen could be written which would give the mass indications of 55, 95 and 110. These masses are present if the 3,4-dichloro-3,4-dimethylhexene dehydrochlorinates.



$$\begin{matrix} C_2H_5-\overset{Cl}{C}-CH_3 \\ | \\ C_2H_5-\underset{Cl}{C}-CH_3 \end{matrix} \longrightarrow 2HCl + \begin{matrix} C_2H_4=C-CH_3 \\ | \\ C_2H_4=C-CH_3 \end{matrix} \quad (7)$$

The unsaturated hydrocarbon would have a parent mass of 110 and strong mass units of 55 and 95. The mass indications of 112 and 97 arise from two sources (a), the unsaturated ketone of reaction (5) and (b) the dimer (3,4-dichloro-3,4-dimethylhexane) less two chlorine atoms.

The mass analysis of the reaction products of mercury dimethyl with *s*-butyl chloride at 300° showed mass units at 55, 95, 110 and the product was found to be



$$\begin{matrix} C_2H_4=C-CH_3 \\ | \\ C_2H_4=C-CH_3 \end{matrix}$$

(If *s*-butyl chloride is heated alone at 300°, only butene-2 and hydrogen chloride are produced.) The methyl radicals from the mercury dimethyl have reacted with the *s*-butyl chloride to form *s*-butyl chloride radicals which dimerized and then dehydrochlorinated.

Partial decomposition of the 3,4-dichloro-3,4-dimethylhexane takes place since a chemical analysis showed only 22.24% chlorine. This chlorine content of the high boiling liquid would require that the dimer be decomposed to the extent of 42.5 to 59% depending upon the degree of decomposition of the *β*-chloro ketone. The final liquid mixture would consist of a *β*-chloro ketone, an alkyl dichloride, an unsaturated ketone and an unsaturated hydrocarbon. All of these products are accounted for in the proposed reaction mechanism.

The high boiling liquid produced in the reaction of *s*-butyl chloride in the presence of photolysis products from acetone turns from a water-white substance to a dark brown liquid upon standing in the presence of hydrogen chloride. This discoloration may be explained as a result of the unsaturated ketone produced in reaction (5) condensing with itself or acetone, catalyzed by the presence of the hydrogen chloride. Each condensation would introduce two conjugate double bonds which soon would be sufficient to produce color.

Changes in the quantum yield of hydrogen chloride result from the thermal instability of the compounds produced in the photoreaction such as the 4-chloro-4-methylhexanone-2, and the 3,4-dichloro-3,4-dimethylhexane.

Acknowledgment.—The mass spectrometer analyses performed by Mr. R. H. Roberts have made parts of this study possible.

The author acknowledges the many helpful discussions and criticisms of Drs. I. B. Johns, R. A. Ruehrwein and Prof. G. B. Kistiakowsky.

DAYTON, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Aromatic Compounds as Donor Molecules in Hydrogen Bonding[1]

BY MILTON TAMRES

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The ability of several substituted benzenes and naphthalenes to behave as donor molecules in hydrogen bonding was investigated by a calorimetric and a spectroscopic method. The study shows that aromatic compounds are capable of forming hydrogen bonds with such molecules as chloroform and methanol-*d*. The association between an aromatic compound and chloroform occurs in a one to one ratio. Halogen substitution in the benzene ring decreases the electron donor ability of aromatic compounds toward hydrogen bonding, whereas methyl substitution increases the electron donor ability. There is some indication, however, that excessive methyl substitution may produce steric interference in the formation of hydrogen bonds with chloroform and with bromoform.

Introduction

The postulation that the aromatic nucleus is an electron donor[2] and, therefore, a Lewis base has received considerable support in recent years. A number of techniques have been developed to measure the relative basicities of aromatic compounds by determining the extent to which they associate with acids. Among the acids reported in the literature may be listed iodine,[3] silver ion,[4] aluminum bromide,[5] hydrogen chloride[6a] and fluoboric acid.[6b] Of these only the last two are proton acids, and they are strong acids.

Numerous studies have shown that weak proton acids can form hydrogen bonds with electron donor molecules. However, the donor molecules most frequently cited are those which contain a fluorine, oxygen or nitrogen atom. Recently, Jones and Badger[7] have reported that aromatic hydrocarbons behave as donor molecules toward methanol. Also, observations in this Laboratory of similar interactions between aromatic compounds and methanol-*d* were pointed out in a previous publication.[8] The present paper reports a more extensive study based upon these initial observations.

Two methods were employed in this investigation. One was a calorimetric method to determine the heats of mixing of aromatic compounds with chloroform, with bromoform and with carbon tetrachloride. The second was a spectroscopic method to determine the effect of aromatic compounds on the frequency shift of the OD band in the infrared spectrum of methanol-*d* solutions. The choice of these techniques, and in particular the use of methanol-*d* rather than methanol was prompted by the fact that there exist in the literature[8–10] data for similar hydrogen bonding studies with other electron donors. By employing the same techniques, then, there is an opportunity for direct comparison of the electron donor ability of aromatic compounds with some of the more well known donor substances.

Experimental

Materials.—The refractive index of each liquid at 20° is given in parentheses for the sodium D line. Measurements were made with a Bausch and Lomb Abbe-56 refractometer.

Chloroform and carbon tetrachloride were purified as specified by Fieser[11]: chloroform (1.4660); carbon tetrachloride (1.4602).

With the exception of benzene, toluene, *o*-xylene and *o*-chlorotoluene which were from the Allied Chemical and Dye Company, all the aromatic compounds were Eastman Kodak Company chemicals. These were dried for several days over calcium chloride and distilled over sodium using a six-inch column with a heated jacket and packed with glass helices. The fraction distilling over a narrow temperature range was taken, the first and last fractions being discarded: 1,2-dichlorobenzene (1.5510); chlorobenzene (1.5246); bromobenzene (1.5588); α-chloronaphthalene (1.6326); *o*-chlorotoluene (1.5255); benzene (1.5009); toluene (1.4968); α-methylnaphthalene (1.6108) (no noticeable change in refractive index after several redistillations); *m*-xylene (1.4964); *p*-xylene (1.4956); *o*-xylene (1.5049); mesitylene (1.4962).

Methanol-*d*, b.p. 64.5–65°, and bromoform (1.5969 at 20.9°) were kindly supplied by Dr. Scott Searles of Northwestern University.

Apparatus and Method.—The apparatus and method employed for the heat of mixing determinations[8] were essentially those described by Zellhoefer and Copley.[12] For the aromatic compounds which gave the highest heats of mixing with chloroform, namely, mesitylene and the xylenes, duplicate determinations were made at 50 mole % chloroform. The results indicate that the values reported are reproducible to within ±4 cal. per mole of solution.

Infrared spectra were determined[8] with a Perkin–Elmer Model 12B spectrometer equipped with a lithium fluoride prism, and calibration of the instrument was made on the rotational fine structure of hydrogen bromide using the grating data of Plyler and Barker.[13]

The spectroscopic method has been described by Gordy and consists of comparing the position of the monomeric OD band in a 0.1 molar solution of methanol-*d* in a reference solvent with the OD band in 1.0 molar solutions of methanol-*d* in various electron donor solvents. Gordy used benzene as his reference solvent, whereas carbon tetrachloride was the reference solvent chosen for this investigation. An example of the infrared spectra obtained is shown in Fig. 1.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1951.

[2] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1939).

[3] (a) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); (b) *ibid.*, **70**, 2832 (1948).

[4] (a) I. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950); (b) *ibid.*, **72**, 3113 (1950); (c) *ibid.*, **71**, 3644 (1949).

[5] R. E. Van Dyke, *ibid.*, **72**, 3619 (1950).

[6] (a) H. C. Brown and J. Brady, *ibid.*, **71**, 3573 (1949); (b) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

[7] L. H. Jones and R. M. Badger, *ibid.*, **73**, 3132 (1951).

[8] S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951).

[9] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

[10] W. Gordy and S. C. Stanford, *ibid.*, **8**, 170 (1940).

[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1935, pp. 308, 309.

[12] G. F. Zellhoefer and M. J. Copley, THIS JOURNAL, **60**, 1343 (1938).

[13] E. K. Plyler and E. F. Barker, *Phys. Rev.*, **44**, 984 (1933).