Summary

The homogeneous thermal decomposition of cyclopentene has been studied in a static system over the temperature range 483–548° at pressures from 38 to 249 mm. Determination of the cyclopentadiene and non-condensable gas in the products has shown that the principal reaction is the dehydrogenation of cyclopentene to cyclopentadiene and that during the early portion of the decomposition the pressure increase is a satisfactory indication of the amount of dehydrogenation. The measurement of $t_{25\%}$ at different initial pressures indicates that the reaction is first order, but during a single run the value of the first order constant calculated from pressure measurements, is not constant in the later stages of the decomposition. The first order rate constant can be expressed as

$$k = 1.10 \times 10^{13} e^{-58,800/RT} \text{ sec.}^{-1}$$

The addition of propylene to cyclopentene does not appreciably alter the rate of pressure increase.

ROCHESTER, NEW YORK RECEIVED JULY 30, 1948

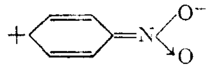
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

Steric Inhibition of Resonance in Chlorinated Benzoic Acids

BY SIDNEY D. ROSS

In connection with other work in this Laboratory, it became important to know whether or not chlorine atoms at the two and six positions of a benzene ring interfered with the reactivity of a substituent at the one position. The published material on the reactions of 2,6-dichlorophenyl and pentachlorophenyl derivatives does not permit a clear-cut decision on this point. Pentachlorobenzaldehyde reacts like a normal unhindered aldehyde. It readily forms an anil, oxime and phenylhydrazone,[1] undergoes the Perkin reaction,[1] and adds a methyl,[1,2] phenyl[1] and allyl Grignard. Pentachloroacetophenone, which we have prepared by oxidation of methylpentachlorophenylcarbinol, does not add methylmagnesium bromide. Yet the methylpentachlorophenylcarbinol reacts readily with thionyl chloride[2] to give the chloride and with hydrogen bromide to give the bromide,[3] and both β-chloroethylpentachlorobenzene[2] and α-bromoethylpentachlorobenzene[3] dehydrohalogenate readily to give pentachlorostyrene. Pentachlorotoluene chlorinates readily to give either the benzyl[4] or benzal chloride[5] but ethylpentachlorobenzene chlorinates[2] preferentially in the β-position although it brominates cleanly in the α-position. 2,6-Dichlorobenzoic acid can be esterified with ethanol in the presence of hydrogen chloride but the rate of esterification is about 1/160 as fast as that for benzoic acid. Furthermore, the ethyl ester reacts with phenylmagnesium bromide but only a 6% yield of the addition product, 2,6-dichlorotriphenylcarbinol is isolated.[6]

We have directed our attention toward obtaining evidence which is independent of what happens in a specific chemical reaction. Ultraviolet absorption spectroscopy has proven to be a convenient tool to this end.[7] The case of steric inhibition of resonance most extensively studied by spectroscopic methods is that of the ortho-substituted nitrobenzenes which have been studied by Sherwood and Calvin,[8] Remington,[9] and most recently by Brown and Reagan.[10] The absorption of nitrobenzene can be attributed to larger contributions to the excited state of the forms



etc.

in which the nitrogen to ring carbon bond has more double bond character. Such a double bond imposes planarity on the entire molecule. If ortho substituents oppose the assumption of a planar configuration the molecule will less frequently be brought to such a configuration and strain will be present when planarity is attained. This strain will increase the energy of the excited state and the corresponding absorption will occur at higher frequencies. Also the probability of excitation and consequently the intensity of absorption will be decreased. Thus the theory of sterically inhibited resonance predicts both de-

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[1] Lock, *Ber.*, **72B**, 300 (1939).

[2] Ross, Markarian and Nazzewski, THIS JOURNAL, **69**, 1914 (1947).

[3] Ross, Markarian and Nazzewski, *ibid.*, **69**, 2468 (1947).

[4] Beilstein and Kuhlberg, *Ann.*, **150**, 302 (1869).

[5] Lock, *Ber.*, **66**, 1527 (1933).

[6] Reich, *Bull. soc. chim.*, [4] **21**, 219 (1917).

[7] Our first approach to the problem was to study the ionization of 2,6-dichloro- and pentachlorobenzoic acid in concentrated sulfuric acid by the technique of Treffers and Hammett (THIS JOURNAL, **59**, 1708 (1937)). Newman (*ibid.*, **63**, 2431 (1941)) has suggested as one explanation for the van't Hoff factor of four in the case of mesitoic acid the steric inhibition of resonance resulting from the fact that the ortho methyl groups interfere with the coplanarity of structures having a double bond between the carboxyl carbon and the ring. If this were the explanation then the van't Hoff factors of substituted benzoic acids in concentrated sulfuric acid would be a useful measure of steric interference about the carboxyl group. For 2,6-dichloro- and pentachlorobenzoic acid we obtained van't Hoff factors of 1.9 and 2.2, respectively. Although our results are of limited reliability because of the very slow solubility of the acids in sulfuric acid and the poor breaks obtained in the temperature–time curves they do suggest to us that stabilization of the acyl ion rather than steric inhibition of resonance is the important requirement in obtaining a factor of four.

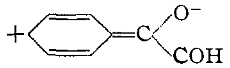
[8] Sherwood and Calvin, THIS JOURNAL, **64**, 1350 (1942).

[9] Remington, *ibid.*, **67**, 1838 (1945).

[10] Brown and Reagan, *ibid.*, **69**, 1032 (1947).

creased intensity and shifts to higher frequencies with increasing hindrance.

The absorption of benzoic acid can be attributed to contributions of the forms


etc.

in which there is interaction between the carboxyl group and the ring.[11] As in the case of the nitrobenzenes, ortho substituents which interfere with the coplanarity of the above contributing structures would be expected to cause a decreased intensity of absorption and a shift to higher frequencies.

We wish at this time to report the ultraviolet absorption spectra in dioxane of three dichlorobenzoic acids, the 3,4-, the 2,4- and the 2,6-dichlorobenzoic acids, and also of pentachlorobenzoic acid, all of which are shown in Fig. 1. 3,4-Dichlorobenzoic acid may be used as a reference compound since both chlorine atoms are sufficiently removed from the carboxyl group to be considered incapable of inhibiting resonance interaction with the ring. This acid absorbs from 280–290 mμ and has an extinction coefficient of 1000 at the maximum. For 2,4-dichlorobenzoic acid the absorption is shifted slightly to shorter wave lengths (273–282 mμ) but the intensity is actually slightly higher (ϵ = 1130 at the maximum) and we therefore conclude that there is no appreciable steric inhibition of resonance in this case. With 2,6-dichlorobenzoic acid the effects of steric hindrance are apparent, for the absorption is shifted to shorter wave lengths (270–280 mμ) and the intensity is greatly decreased (ϵ = 400 at the maximum). It is of interest that as a result of this steric effect the spectrum of 2,6-dichlorobenzoic acid is very similar to that of the dichlorobenzenes which absorb from 270–280 mμ and have an extinction coefficient of 400 at the maximum.[12] With pentachlorobenzoic acid any shift due to steric effects is obscured by the greater mass of this acid which results in absorption at longer wave lengths, and, as a result, 3,4-dichlorobenzoic acid is an unsatisfactory reference compound. However, the low intensity (ϵ = 390 at the maximum) definitely indicates steric hindrance. The infrared spectra of two of these acids, 2,4-dichlorobenzoic acid and 2,6-dichlorobenzoic acid, have been measured at the Sloan–Kettering Institute for Cancer Research.[13] The former shows carbonyl absorption at 1707 cm.$^{-1}$ and the latter at 1724 cm.$^{-1}$. This shift to a higher frequency in going from the 2,4- to the 2,6-acid indicates that the carbonyl group is more double bonded in the 2,6-acid and is further evidence for the fact that the carboxyl group ring interaction is suppressed in this case.

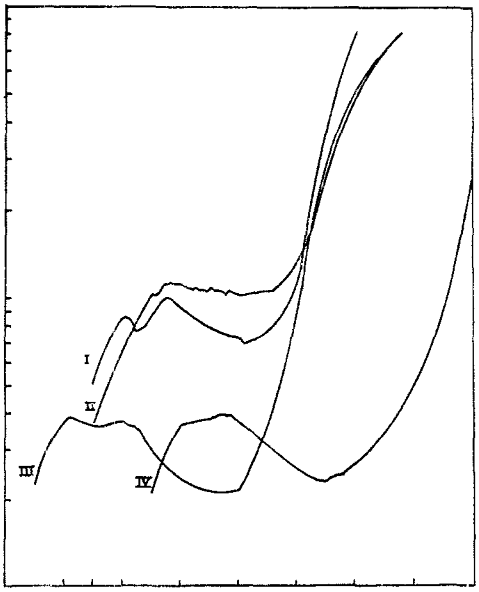


Fig. 1.—Ultraviolet absorption spectra of chlorinated benzoic acids in dioxane; I, 3,4-dichlorobenzoic acid; II, 2,4-dichlorobenzoic acid; III, pentachlorobenzoic acid; IV, 2,6-dichlorobenzoic acid.

From the above it is clear that when two ortho chlorine substituents are present steric hindrance becomes an important consideration. Furthermore, if we consider the reactions cited earlier in this paper it seems reasonable to assume that when the substituent at the one position is small in size even two ortho chlorine atoms may not introduce appreciable steric hindrance. Kadesch and Weller[14] have found from dipole moment measurements that steric hindrance obtains in the case of acetylmesitylene but not in the case of mesitaldehyde, and it is on this basis that we would explain the ready addition of a Grignard reagent to pentachlorobenzaldehyde and its failure to add to pentachloroacetophenone.

Acknowledgment.—The author wishes to express his indebtedness to Dr. John D. Roberts for the absorption spectra reported herein, to Dr. Seymour Lieberman for permission to use the infrared data, and to Drs. Preston Robinson and John Burnham for many helpful discussions.

Experimental[15]

Allylpentachlorophenylcarbinol.—Pentachlorobenzaldehyde (112 g., 0.4 mole) was added to the Grignard reagent prepared in the usual manner from magnesium (14.6 g., 0.6 mole) and freshly distilled allyl bromide (78.5 g., 0.65 mole). The addition complex was decomposed with ice, ammonium chloride and aqueous acetic acid. The product was extracted with ether. The ether extract was dried and the solvent was removed to yield 127 g. (99%) of the crude carbinol melting from 99–106°. Recrystallization from methanol–water gave 90 g. melting from 111–112.5°. A sample recrystallized two additional times for analysis melted from 112–113°.

Anal. Calcd. for $C_{10}H_7OCl_5$: C, 37.47; H, 2.18. Found: C, 37.51, 37.34; H, 1.98, 2.12.

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(11) Kumler and Strait, THIS JOURNAL, **65**, 2349 (1943).

(12) Wolf and Herold, *Z. physik. Chem.*, **B13**, 201 (1931).

(13) We are indebted to Dr. S. Lieberman, Dr. K. Dobriner and Mrs. Phyllis Humphries of the Sloan–Kettering Institute for the determination and interpretation of these infrared spectra

(14) Kadesch and Weller, THIS JOURNAL, **63**, 1310 (1941).

(15) The microanalyses were performed by Dr. Carl Tiedcke.

Pentachloroacetophenone.—Pentachlorophenyl methyl carbinol (118 g., 0.4 mole) was dissolved in one liter of glacial acetic acid, heated to the boiling point. Chromic anhydride (40 g., 0.4 mole) was added in three portions without further heating. The reaction mixture was left standing overnight and then poured into a large volume of water. The crude product was filtered and crystallized from ethanol to yield 97 g. (82.7%) of the ketone melting from 88–90°. A sample recrystallized from ethanol for analysis melted from 90–92°.

Anal. Calcd. for $C_8H_3OCl_5$: C, 32.81; H, 1.03. Found: C, 32.48, 32.60; H, 1.24, 1.16.

When pentachloroacetophenone in ether solution was added to an ether solution of methylmagnesium bromide no addition took place and the ketone was recovered unchanged.

Chlorinated Benzoic Acids.—The chlorinated benzoic acids were all prepared by oxidation of the corresponding aldehydes with alkaline potassium permanganate. In a typical experiment 2,4-dichlorobenzaldehyde (50 g., 0.285 mole), potassium permanganate (33.5 g., 0.194 mole) and sodium carbonate (60 g., 0.434 mole) in two liters of water was refluxed for three hours. The aqueous solution was filtered, cooled, extracted with benzene to remove unreacted aldehyde and finally acidified with sulfuric acid to yield the crude acid, having m. p. 158–160°. Recrystallization to a constant melting point from ethanol–water gave 40 g. (72%) of the acid melting at 160°. This agrees with the melting point of 159–160° previously reported by Cohen and Dakin[16] but Bornwater and Holleman[17] have reported the higher melting point of 164.3°. 3,4-Dichlorobenzoic acid was also crystallized from ethanol–water and melted from 207.5–209°. The highest previous melting point reported for this compound is 204.1°.[17] 2,6-Dichlorobenzoic acid, recrystallized by covering it with ligroin (b. p. 70–90°) and then adding benzene dropwise while boiling until the acid just went into solution, melted from 143–144°. Bornwater and Holleman[17] report a melting point of 143.7° for this compound. Pentachlorobenzoic acid was recrystallized from benzene and melted from 209.6–210.5°. Lock[1] has reported a melting point of 208° for pentachlorobenzoic acid. The absorption spectra in dioxane were measured by Dr. John D. Roberts using a Beckman spectrophotometer. Each sample was run at three concentrations and only those values of the transmission were retained which fell between 15 and 80%.

Summary

The ultraviolet absorption spectra of four chlorinated benzoic acids are reported. The decreased intensity, observed in the case of the di-ortho substituted acids, is attributed to suppression of the carboxyl group resonance.

[16] Cohen and Dakin, *J. Chem. Soc.*, **79**, 1129 (1901).

[17] Bornwater and Holleman, *Rec. trav. chim.*, **31**, 227 (1912).

NORTH ADAMS, MASS. RECEIVED JUNE 16, 1948

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

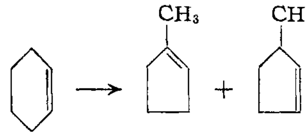
Isomerization of Cyclohexenes to Cyclopentenes: Oxidation of These Alkenes to Glycols and Acids

BY HOMER ADKINS AND ALAN K. ROEBUCK[1]

Zelinsky and Arabuzov[2] reported the isomerization of cyclohexene to methylcyclopentenes over alumina. The process seemed to offer a route for the preparation, from available cyclohexenes, of several cyclopentenes, glycols and acids, of possible value in organic syntheses. While our study was interrupted in the period 1942–1945, inclusive, several papers bearing on the subject appeared. Among these may be noted that of Block and Thomas[3] and an even more helpful publication by Scanlan, Swern, Billen and Findley.[4] The application of their method for oxidizing alkenes to glycols with hydrogen peroxide in formic acid has proven most useful.

We were fortunate in choosing as a catalyst pure alumina,[5] prepared from distilled aluminum isopropoxide, thus avoiding the multiplicity of reactions induced by the cracking catalyst used by Block and Thomas. The pure alumina catalyst was almost ten times as active per unit volume as one of the standard commercial alumina catalysts. The alumina *ex*-aluminum isopropoxide was quite active in isomerizing cyclohexenes to cyclopentenes. It was also active in establishing equilibrium between hydrocarbons differing only in the position of a double bond. The catalyst was not active, in converting cyclopentenes to cyclohexenes, to a significant extent, under the conditions described.

Cyclohexene (I) was isomerized, over alumina at 470–480°, to 1-methylcyclopentene-1 (II) and 1-methylcyclopentene-2 (III), in a ratio of about 2.5 to 1. In a typical experimental 800 ml. of cyclohexene was passed over 120 ml. of the granular alumina catalyst at a rate of 60–70 ml. per hour. The reaction product (788 ml.) gave after fractionation 328 ml. of I, 273 ml. of II and 108 ml. of III.



I II III

Methylcyclohexene-1 (IV) was isomerized to 1,2-dimethylcyclopentene-2 (V) and 1-ethylcyclopentene-2 (VI). The yields of V and VI, on the basis of the amount of IV reacting, were 17 and 13%, respectively. The isomeric compounds with the unsaturation in the 1-position were also produced but the fraction containing them could not

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[1] Holder of a fellowship in 1946 and 1947 supported by the Standard Oil Co. of Indiana.

[2] Zelinsky and Arabuzov, *Compt. rend. acad. sci.* (*U. R. S. S.*), **23**, 794 (1939); *Chem. Abst.*, **34**, 3696 (1940).

[3] Block and Thomas, THIS JOURNAL, **66**, 1589 (1944).

[4] Swern, Billen, Findley and Scanlan, *ibid.*, **67**, 1786 (1945).

[5] Adkins, *ibid.*, **44**, 2179 (1922).