[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Cyclopentene[1]

BY DON W. VANAS[2] AND W. D. WALTERS[3]

In a study of the homogeneous thermal decomposition of cyclopentene in a flow system Rice and Murphy[4] observed that at 850° with a pressure of 10 mm. and a contact time sufficient to produce about 20% decomposition 0.96 mole of hydrogen and 0.93 mole of cyclopentadiene are formed from each mole of cyclopentene decomposed. In addition, only small amounts of ethylene, propylene, and either allene or methylacetylene were found. From an experiment in a static system at 552° Kuchler[5] reported that 80% of the products of less than five carbon atoms consisted of hydrogen. Presumably the extent of decomposition in this experiment was large so that substances other than the primary products might have been present. A variety of gaseous products were observed in the catalytic thermal decomposition of cyclopentene,[6] but hydrogen still was found to be the gas present in largest amount. Cyclopentene can be transformed catalytically also into cyclopentadiene and cyclopentane.[7] The present investigation which is part of a general study of the thermal decomposition of ring compounds was undertaken to obtain more information concerning the homogeneous thermal decomposition of cyclopentene in a static system.

Experimental

Materials.—The cyclopentene employed in most of the experiments was obtained in 5-ml. glass ampoules (sealed *in vacuo*) from the National Bureau of Standards. This material designated as Standard Hydrocarbon Sample No. 288-5s had a stated purity of 99.966 ± 0.021 mole per cent. In some of the experiments a sample of cyclopentene from the Farchan Research Laboratories was used. The Farchan cyclopentene was fractionated through an 80 cm. Lecky-Ewell column at a reflux ratio of about 20:1. By the use of a very slow stream of dry 99.99% nitrogen during fractionation the cyclopentene was kept out of contact with air. Only a middle fraction (approximately 25%) which boiled at 43.4°, constant to within the precision of the thermometer ±0.2°, at a barometric pressure of 745 mm. was retained. One portion of this middle fraction was used without further treatment. In order to remove any traces of halogen compounds, peroxides, and water another portion of the middle fraction was treated with silver oxide, anhydrous calcium sulfate, and freshly distilled sodium. During this purification process the material was subjected to several trap to trap distillations under vacuum.

The method of preparation of nitric oxide has been described previously.[8] Although the C.P. propylene, which was obtained from the Ohio Chemical Company, did not reveal the presence of any non-condensable gases, it was condensed in liquid air and pumped under high vacuum in an attempt to ensure the complete absence of non-condensable gases, particularly oxygen. To prepare cyclopentadiene for use in the analytical procedure, dicyclopentadiene from the Koppers Company was cracked and fractionated in a 70-cm. column packed with glass helices. The monomer thus prepared was dimerized by refluxing on a steam-bath and then the dimer was distilled under vacuum. The pure dimer obtained as the middle fraction was stored under nitrogen. When needed, the dimer was cracked and fractionated in a 38-cm. column packed with glass beads and small cylinders. The monomer was subjected to several trap-to-trap distillations under vacuum, thoroughly outgassed, and maintained at −78° until used.

Apparatus and Method.—The Pyrex reaction vessel and furnace were a modification of an apparatus already described.[8] The temperature in most cases was measured by the use of a chromel–alumel thermocouple located at the center of the reaction vessel. This thermocouple, which could be connected to a Leeds and Northrup Type K-2 potentiometer, was standardized at frequent intervals against a platinum, platinum–13% rhodium thermocouple which was calibrated at the melting points of zinc and aluminum in accordance with the procedure recommended by the National Bureau of Standards.[9] In the experiments with the Farchan cyclopentene, the platinum, platinum–rhodium thermocouple was used directly to measure the temperature. A temperature control of ±0.1° was obtained by means of a second chromel–alumel thermocouple located at the inside surface of the steel cylinder surrounding the reaction vessel and in contact with the top edge of the reaction vessel. This second thermocouple was connected to the potentiometer, and the light reflected from the mirror of a galvanometer in the thermocouple-potentiometer circuit was used to actuate a photoelectric cell which controlled a small amount of the heating current. From a consideration of the temperature control, calibration and temperature uniformity of the reaction vessel, it is estimated that the absolute accuracy of the temperature measurements should be at least ±0.5°.

The packed reaction vessel, which contained thin-walled Pyrex tubes, had a surface to volume ratio of approximately 28 times that of the unpacked vessel. An unheated mercury manometer was used for the pressure measurements in the majority of the experiments, but in certain experiments the mercury manometer and external capillary tubing were wound with resistance wire and electrically heated. Within the limits of experimental error the same results were obtained with and without heating. In the experiments at the lowest temperature, the external capillary tubing and the manometer were flamed and subjected to prolonged pumping between runs in order to remove compounds of low volatility which might be left in the capillary tubing when the products are removed. In addition, in the same experiments the cyclopentene vapor confined in the reaction vessel was not allowed to come into contact with stopcock grease. This procedure was adopted in order to prevent any loss of cyclopentene vapor during a run. When new, or after contact with air, the reaction vessel was flushed several times with cyclopentene at an elevated temperature. To separate the cyclopentene storage bulb from the vacuum system ordinarily a Warrick–Fugassi valve[10] was used. The cyclo-

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[1] In part from a thesis submitted by Don W. Vanas to the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] A portion of this work was supported by the Office of Naval Research under Contract N6onr-241, Task Order I with the University of Rochester.

[4] Rice and Murphy, THIS JOURNAL, **64**, 896 (1942).

[5] Kuchler, *Z. physik. Chem.*, **B53**, 307 (1943).

[6] Greensfelder and Voge, *Ind. Eng. Chem.*, **37**, 983 (1945).

[7] Plate and Batuev, *J. Gen. Chem.* (*U. S. S. R.*), **16**, 805 (1946); Plate, *ibid.*, **15**, 156 (1945).

[8] Klute and Walters, THIS JOURNAL, **67**, 550 (1945).

[9] Roeser and Wensel, *J. Research Natl. Bur. Standards*, **14**, 247 (1935).

[10] Warrick and Fugassi, *Ind. Eng. Chem., Anal. Ed.*, **15**, 13 (1943).

pentene was out gassed before every experiment. A mercury diffusion pump and an oil pump of the usual type were employed for evacuating the system.

Analyses.—That cyclopentadiene is a principal product of the decomposition in a static system was indicated by that fact that the ultraviolet absorption spectrum of the condensable products at low percentages of decomposition corresponded to that for cyclopentadiene. Moreover, the products reacted with alkaline benzaldehyde to produce the characteristic yellow color of phenylfulvene.[11] To determine the cyclopentadiene and non-condensable gases in the products, the charge after the desired time of reaction was removed from the reaction vessel by expansion through a trap and two spirals immersed in liquid nitrogen and into a series of evacuated bulbs. Approximately 95% of the material in the reaction vessel could be removed almost instantaneously by this method, and since the amount remaining in the reaction vessel was measured, a correction could be applied for the unremoved portion. To ensure complete removal of all condensable substances the gases in the evacuated bulbs were compressed back into the trap and spirals cooled in liquid nitrogen. The non-condensable gas was then removed by the use of a Toepler pump and the volume of the non-condensable gas determined by measurement of the temperature and pressure of the gas in a calibrated gas buret. By removal of the liquid nitrogen from the spirals all the condensable material was distilled into the trap. Absolute alcohol was added to the trap and then the trap was allowed to warm to room temperature. The solution was then diluted to volume with absolute alcohol and an aliquot portion of this solution taken for further dilution with absolute alcohol. In all experiments, except one, the cyclopentadiene was determined by measurement of the optical density at 240 mμ with a Beckman spectrophotometer using absolute alcohol as a reference liquid.[11]

Although the undecomposed cyclopentene has a small absorption at 240 mμ, experiments and calculations which were carried out to determine the amount of absorption showed that the correction for absorption of cyclopentene is negligible in the present experiments. The analytical method was calibrated against pure cyclopentadiene, and in the range of concentrations employed in this study the optical density at 240 mμ was found to be proportional to the concentration. The recovery of cyclopentadiene and the analytical procedure were also checked by placing pure cyclopentadiene in the heated reaction vessel and removing it in the same manner as that used for the products. The accuracy of the method for removal and analysis of cyclopentadiene should be about ±3–4%. Another method of analysis which was used in one experiment involved the reaction of cyclopentadiene with benzaldehyde in alcoholic alkali to form the highly colored phenylfulvene.[11] The optical density of the solution at 400 mμ was determined with the Beckman spectrophotometer against a blank containing the reagents. The calibration curve used in this determination was obtained using known amounts of pure cyclopentadiene. The results obtained by the ultraviolet absorption method and the phenylfulvene method were in agreement.

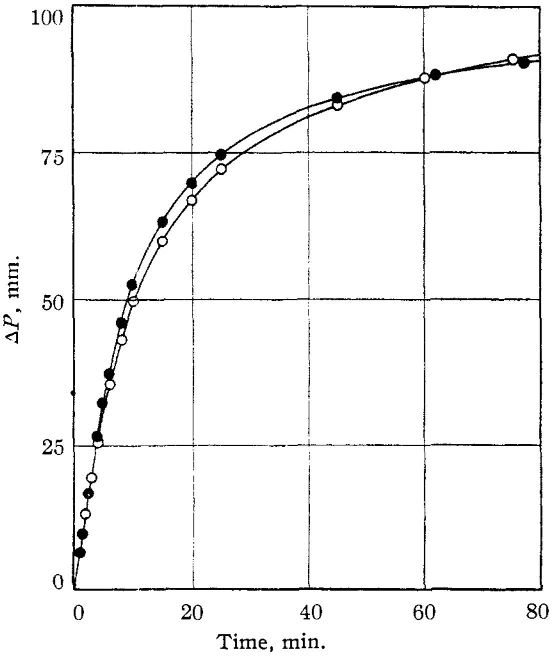

Fig. 1.—Pressure–time curve for cyclopentene decomposition: ●, unpacked bulb, P_0 = 120.5 mm., T = 530.3°; ○, packed bulb, P_0 = 120.2 mm., T = 529.7°.

Results and Discussion

Pressure–Time Curve.—The type of pressure–time curve which is obtained in the decomposition of cyclopentene is shown in Fig. 1. In contrast to the results observed with tetrahydrofuran[12] and cyclopentane[5] the rate of pressure increase at the start of the cyclopentene decomposition corresponds to the behavior expected for a first order reaction. The ratio of the final pressure, p_f, to the initial pressure, p_0, was determined in several experiments and the values obtained are given in Table I. The values shown have been corrected for the small amount of "dead space" in the reaction system outside the furnace.[13] The ratio appears to be close to 2, indicating two molecules of products for each molecule of cyclopentene decomposed. The fact that the value is slightly lower than 2 may be due to reactions in the later stages of the decomposition involving the products. From the results shown it would not be unexpected if the value of p_f/p_0 increases slightly at lower initial pressures and at higher temperatures.

TABLE I

RATIO OF FINAL PRESSURE (p_f) TO INITIAL PRESSURE (p_0)

Temp., °C.	p_0, mm.	p_f/p_0
547.5	63.6	1.95
548.0	121.7	1.89
530.3	120.5	1.86
529.7	120.2[a]	1.88[a]

[a] Packed vessel, 28-fold increase in surface to volume ratio.

Homogeneity.—The data from the experiments in the reaction bulb with increased surface are given in Tables I and II and in Fig. 1. The over-all pressure–time curve in the packed vessel shown in Fig. 1 is very close to that obtained in the unpacked vessel, taking into consideration a slight difference in temperature. Likewise the values of p_f/p_0 (Table I) and the times for 25% pressure increase ($t_{25\%}$ in Table II) in the packed vessel do not differ significantly from the values found in the experiments in un-

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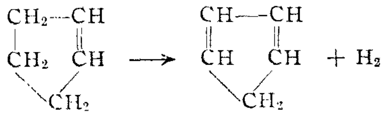
(11) Uhrig, Lynch and Becker, *Ind. Eng. Chem., Anal. Ed.*, **18**, 550 (1946).

(12) Klute and Walters, THIS JOURNAL, **68**, 506 (1946).

(13) Allen, *ibid.*, **56**, 2053 (1934).

packed vessel at comparable temperatures and pressures. These results show that the decomposition of cyclopentene under the conditions used in the present study proceeds homogeneously.

Analyses.—The results of the analyses of the products are shown graphically in Fig. 2. If one molecule of cyclopentene decomposes to form one molecule of cyclopentadiene and one molecule of hydrogen, it would be expected that the pressure of cyclopentadiene in the reaction vessel after some decomposition has occurred would be equal to the pressure of non-condensable gas and also equal to the observed pressure increase. In Fig. 2 the pressure of cyclopentadiene and the pressure of non-condensable gas are plotted against the pressure increase which has occurred during the time the cyclopentene has been in the reaction bulb. It is evident that the amounts of cyclopentadiene during the early stages of the decomposition are approximately equal to the amounts of non-condensable gas, and since most of the points lie close to the 45° straight line, the pressure of either cyclopentadiene or non-condensable gas is about the same as the pressure increase. These results, together with the data mentioned previously, indicate that under the experimental conditions employed in this study the homogeneous decomposition of cyclopentene proceeds chiefly according to the equation



Moreover, during the initial stages of the reaction the pressure increase appears to be a reliable indication of the rate of formation of cyclopentadiene and hydrogen. On account of the possibility of the occurrence of reactions involving the products, it is probable that in the later stages of the reaction the cyclopentadiene pressure will be smaller than the pressure increase and the amount of non-condensable gas will be higher, particularly if methane is formed. There is some indication of such a trend in the data shown in Fig. 2.

Kinetics.—In view of the analytical results, it appeared that pressure measurements could be used satisfactorily to determine the rate of decomposition during the early portion of the reaction. The results of a number of experiments at different pressures and temperatures are summarized in Table II. The value recorded as $t_{25\%}$ represents the time in minutes required for the pressure to increase to 1.25 × p_0. According to the data shown in Fig. 2, for an initial pressure of 110 mm. $t_{25\%}$ also will correspond to approximately 25% conversion of cyclopentene into cyclopentadiene. $t_{25\%}$ was chosen rather than $t_{50\%}$ to avoid as much as possible reaction of or interference by the products. From the fact that at a given temperature the value of $t_{25\%}$ is almost constant over the pressure range 40–250 mm., it ap-

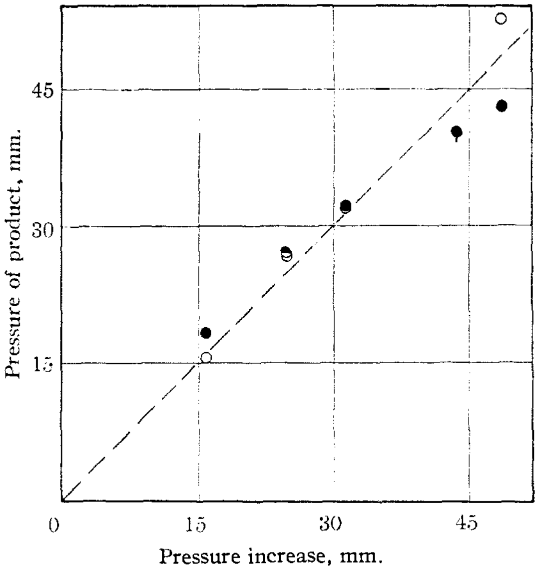


Fig. 2.—Thermal decomposition of cyclopentene at 531°. Cyclopentadiene: ultraviolet absorption, ●; phenylfulvene method, ◓; non-condensable gas, ○; initial pressure, 110 mm. except ●, 80 mm.

TABLE II

RATE OF DECOMPOSITION OF CYCLOPENTENE

Temp., °C.	p_0, mm.	$t_{25\%}$, min.	$k_{(1st\ ord.)}$ × 10, min.$^{-1}$
482.8	119.8	44.3	0.0649
482.8	142.6	43.6	.0660
495.1	122.2	23.7	.121
495.0	122.3	23.3	.123
518.9	58.4	7.03	.409
519.0	79.3	6.71	.429
519.0	110.6	6.86	.419
519.1	119.4	7.15	.402
519.1	249.3	8.13	.354
529.5	111.6	4.53	.635
529.6	120.1[a]	4.97[a]	.579[a]
529.7	120.2[a]	4.88[a]	.590[a]
530.3	120.5	4.63	.621
530.6	53.5	3.67	.784
531.2	80.0	4.05	.710
531.2	119.7	3.98	.723
531.2	58[b]	3.74[b]	.769[b]
531.2	110[b]	3.83[b]	.751[b]
531.2	108[c]	3.90[c]	.738[c]
531.1	242[b]	4.09[b]	.703[b]
547.4	37.5	1.89	1.52
547.3	49.8	1.81	1.59
547.4	60.6	1.70	1.69
547.5	63.5	1.98	1.45
547.4	82.3	1.94	1.48
548.1	119.7	1.98	1.45
548.0	121.6	1.96	1.47

[a] Packed vessel. [b] Farchan cyclopentene, fractionated and treated; average of two runs. [c] Farchan cyclopentene, fractionated; average of two runs. Except in experiments marked "b" and "c" cyclopentene from the National Bureau of Standards was employed.

pears that the dehydrogenation of cyclopentene is a first order reaction. Likewise the initial slope of the pressure–time curve was found to be proportional to the initial pressure, within the limits of experimental error. There appears to be a small increase in the value of $t_{25\%}$ as the initial pressure is increased from lower (40–60 mm.) to higher pressures (240–250 mm.). Since $t_{25\%}$ depends upon pressure measurements, this apparent increase in the quarter life may not be real and may be due to the same factors which cause the value of p_f/p_0 to decrease slightly with increasing pressure.

The data in Table II reveal no significant difference in the rates of decomposition of the different samples of cyclopentene. The values of k given in Table II were calculated from $t_{25\%}$ on the basis that the decomposition is first order. The calculation of first order rate constants during a single run from pressure measurements and the over-all pressure increase indicates that the value of the rate constant remains reasonably constant during the first quarter of the decomposition; but by about 40% decomposition the value has decreased by 10%, and after this time the value continues to fall off. In view of the analyses for cyclopentadiene and non-condensable gas at the largest amounts of decomposition shown in Fig. 2, it is probable that reactions other than the dehydrogenation of cyclopentene occur as the products accumulate and that the measurement of pressure may not be a satisfactory indication of the amount of decomposition in the later portion of the reaction. It would be desirable to have analyses for the undecomposed cyclopentene in order to calculate the rate of disappearance of cyclopentene during the entire course of the reaction.

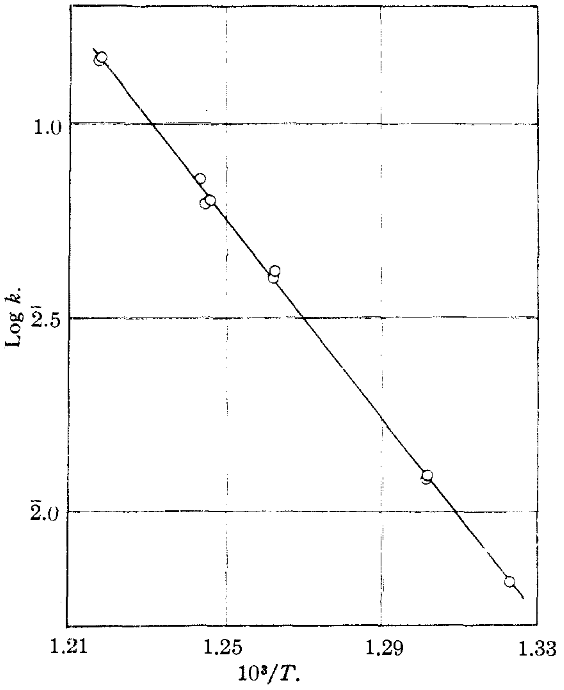


Fig. 3.

The increase in the reaction rate with increasing temperature is shown graphically in Fig. 3, in which a plot of log k *vs.* $1/T$ is given. The data shown in this diagram represent more than a twenty-fold increase in rate constant over the temperature interval from 483 to 548°. For this plot only runs in the neighborhood of 110–120 mm. initial pressure (with N.B.S. cyclopentene) have been used since there may be a small change in $t_{25\%}$ with initial pressure. Moreover, in the previously mentioned runs with initial pressures of 110 mm. the analyses showed that $t_{25\%}$ corresponds closely to 25% conversion into products. An activation energy of 58.8 kcal. was obtained from the slope of the line in Fig. 3, and by the use of this activation energy the reaction rate constant can be expressed as

$$k = 6.6 \times 10^{14}\, e^{-58.800/RT} \text{ min.}^{-1}$$

or

$$k = 1.10 \times 10^{13}\, e^{-58.800/RT} \text{ sec.}^{-1}$$

Mechanism.—In an attempt to determine whether or not the dehydrogenation of cyclopentene proceeds by means of a free radical chain mechanism, preliminary experiments were carried out in the presence of added nitric oxide. The addition of either 1 mm. or 5 mm. of nitric oxide to 110 mm. of cyclopentene at 529.5° gave no noticeable inhibition. Similarly the addition of 51 mm. of propylene to 100–110 mm. of cyclopentene at 531° produced no change in the rate of pressure increase. Therefore, it appears that these experiments do not offer any evidence for the existence of a free radical chain mechanism. From the results mentioned above and the fact that during the early stages of the decomposition before the products accumulate the reaction seems to be first order, it might be assumed that the dehydrogenation is a unimolecular reaction. Likewise the frequency factor in the rate expression is of the order of magnitude expected for a unimolecular reaction. Rice and Murphy[4] have discussed two possible mechanisms for the dehydrogenation of cyclopentene: (a) separation of molecular hydrogen in a single elementary step and (b) a hydrogen atom chain mechanism. In his discussion of the homogeneous thermal decompositions of alicyclic hydrocarbons Eucken[14] assumed that the dehydrogenation of cyclopentene is a unimolecular reaction in which the hydrogen atoms of two neighboring CH_2 groups combine directly with each other to form a hydrogen molecule. Although at present the dehydrogenation of cyclopentene appears to be unimolecular, in view of the complexity of many apparently simple reactions it seems well not to draw a definite conclusion about the mechanism until further investigations are carried out.

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(14) Eucken, *Die Chemie*, **56**, 342 (1943).

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

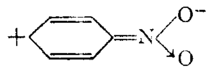
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

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).