librium was shifted by removing formaldehyde with hydroxylamine hydrochloride; eventually all of the monomethylolurea was consumed, and a molecular equivalent of hydrochloric acid was liberated. This method was used to determine the amount of combined formaldehyde in monomethylolurea.

NEWARK, DELAWARE RECEIVED APRIL 28, 1948

[CONTRIBUTION FROM COATES LABORATORIES, LOUISIANA STATE UNIVERSITY]

Kinetics of the Thermal Decomposition of Isopropyl Chlorocarbonate

BY ARTHUR R. CHOPPIN AND EDGAR L. COMPERE

Earlier investigations by the senior author[1,2] have shown that the gas phase thermal decomposition of ethyl chlorocarbonate, which was studied at 150–200°, is homogeneous and unimolecular. It follows the equation

$$C_2H_5OCOCl \longrightarrow C_2H_5Cl + CO_2$$

The decomposition has been shown to occur without side reactions and a mechanism of internal rearrangement was proposed. The rate constant is given by the equation

$$k = 5.5 \times 10^{10}e^{-29410/RT}$$

This reaction appears to be one of the few uncomplicated gas reactions known, and as such furnishes valuable data for testing theory. From this viewpoint the investigation of the behavior of homologous compounds would be of interest.

Ramsperger and Waddington[3] observed that trichloromethyl chlorocarbonate decomposed into two molecules of phosgene. The reaction was found to be first order, and only a slight degree of heterogeneity was noted. The first order rate constant is given by the equation

$$k = 1.4 \times 10^{13}e^{-41500/RT}$$

The only other investigation of the kinetics of chlorocarbonate decomposition is that of Lessig,[4] who reports two rate determinations in a constant volume apparatus on isobutyl chlorocarbonate. At 267° he observed a half life of 160 min. and a $^3/_4$ life of 380 min. At 302° a half life of 16 min. and a $^3/_4$ life of 35 min. was reported. The final pressure was more than twice the initial, indicating decomposition into more than two particles. A graph, in which time was plotted against the logarithm of the difference between final and observed pressures, gave a straight line, indicating a first order reaction. From these data an approximate equation for the first order rate constant may be developed

$$k = 1 \times 10^{13}e^{-40000/RT}$$

Other chlorocarbonates decompose to yield a variety of products. Merck[5] has reported that tertiary amyl chlorocarbonate decomposed at room temperature with evolution of gas. Choppin and Rogers[6] found that liquid α-phenylethyl chlorocarbonate decomposed, when held at 100° for a short time, yielding α-phenylethyl chloride, carbon dioxide, styrene and hydrogen chloride. Aromatic chlorocarbonates decompose into phosgene and the aromatic carbonate, according to Bowden.[7]

It is planned to investigate the decomposition kinetics of various chlorocarbonates. Methyl, ethyl, isopropyl and tertiary butyl chlorocarbonate are of particular interest since they permit a study of the effect of increased methylation of the alpha carbon atom. This paper reports a study of the kinetics of the thermal decomposition of isopropyl chlorocarbonate.

Experimental

Eastman Kodak Co. isopropyl chlorocarbonate was purified by fractionating at 200 mm. pressure through a 40-inch adiabatic glass column packed with $^5/_{32}$ inch glass helices. A fraction taken between 66–67° was treated several hours with phosphorus pentoxide. This treatment, which is believed to remove alcoholic impurities, was necessary in order to obtain a high final purity in the chlorocarbonate. The treated cut was redistilled, and the middle portion of a fraction boiling at 66.3° (200 mm.) was used in this investigation. Analysis of this material for chlorine indicated a purity of 99.4% or better. Isopropyl carbonate, b. p. 147°,[8] found as an impurity in the original sample boiled at 102.6° at 200 mm. pressure.

The decomposition was first studied in the static apparatus described elsewhere[1,9] in which the decomposition is followed by observing pressure changes in an all-glass system. Decomposition was observed at 220–232°. Graphs of time *versus* the logarithm of the difference between final pressure and observed pressure, gave good straight lines, which indicated a first order reaction. A curvature of the plot during the early part of the run possibly indicated a more rapid initial rate, but it was difficult to separate this effect from that due to temperature rise occurring as the reaction vessel was immersed in the thermostat to initiate the reaction.

The results of the various static runs are summarized in Table I. An examination of the data indicates that the ratio of initial to final pressures is always greater than two, but is relatively constant between 2.45 and 2.52. This would indicate that more than two reaction products were present and that probably two or more reaction mechanisms were also involved in the decomposition. The last two runs which were made in cells packed with glass wool show a materially increased rate constant indicating a cata-

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(1) A. R. Choppin, H. A. Frediani and G. F. Kirby, THIS JOURNAL, **61**, 3176 (1939).

(2) A. R. Choppin and G. F. Kirby, *ibid.*, **62**, 1592 (1940).

(3) H. C. Ramsperger and G. Waddington, *ibid.*, **55**, 214 (1933).

(4) E. T. Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).

(5) E. Merck, German Patent 254,471 (1913).

(6) J. W. Rogers, Master's Thesis, Louisiana State University, 1942.

(7) S. T. Bowden, *J. Chem. Soc.*, 310 (1939).

(8) P. N. Kogerman and J. Kranig, *Chem. Abst.*, **21**, 1729 (1927).

(9) F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1939.

lytic wall effect with at least one of the reaction mechanisms being heterogeneous.

TABLE I

DECOMPOSITION RATE OF ISOPROPYL CHLOROCARBONATE IN STATIC APPARATUS

Temp., °C.	Calcd. initial pressure, mm.	Pressure ratio initial/final	First order rate constant, $k \times 10^4$ sec.$^{-}$
220	...	..	3.0
221	177	2.45	7.7
221	232	2.45	5.4
232	270	2.46	..
232	216	2.48	..
232	266	2.48	26
232	194	2.46	21
232	138	2.52	55[a]
232	...	..	53[a]

[a] Reaction cell packed with glass wool in these runs.

In order to identify the reaction products, weighed samples of isopropyl chlorocarbonate were decomposed in sealed bulbs immersed several hours in a thermostat at 220°. Isopropyl chloride was isolated by condensing it in a small tip of the bulb immersed in Dry Ice, and identified by boiling point at atmospheric pressure, approximately 35°. Carbon dioxide and propylene were identified and estimated in a Fisher gas analysis apparatus. Both acid absorption and combustion techniques were used on the propylene. No gas residue remained after the carbon dioxide and propylene were absorbed. Based on the original chlorocarbonate, 96–102 mole per cent. of carbon dioxide and 65 mole per cent. of propylene were found. Propylene was further identified in another experiment by conversion to the dibromide, b. p. 143° (760 mm.), (literature 141.6°). Hydrogen chloride was shown in subsequent flow experiments to be an additional decomposition product.

These experiments indicated that two reactions occur, so that study in a flow system was desirable. In such a system analysis might be made simultaneously for several constituents of the reaction mixture. The decomposition rate was determined by vaporizing isopropyl chlorocarbonate into a metered stream of dry nitrogen gas, passing the mixture through a thermostatted reaction tube, and analyzing the emergent mixture for carbon dioxide, hydrogen chloride, and unreacted chlorocarbonate.

The first part of the flow system consisted of a cylinder of nitrogen gas followed by four bubblers, three containing Fieser[10] solution to remove oxygen and one containing lead acetate for hydrogen sulfide removal. Next, two sulfuric acid bubblers were followed by a pressure regulator, a flow meter and a manometer. Between the manometer and the reaction tube were two thermostatted bubblers of isopropyl chlorocarbonate. The temperatures of the isopropyl chlorocarbonate containers were adjusted so as to give a predetermined vapor pressure for the chlorocarbonate. The entire system was calibrated so as to maintain a constant flow against a definite pressure head as follows: One arm of the three-way stopcock at the end of the reaction tube was connected to the analytical train. The other arm was bent downward and immersed in water. By suitably adjusting the depth of the water a flow resistance was created equal to that of the analytical train. In this way the same flow rate was maintained through either outlet of the system. The water outlet was used in the first part of the experiment, while a steady state of decomposition was being attained.

Two reactors were used at different times in the investigation. The larger was a 270-cm. coil of 6.0-mm. bore Pyrex tubing, with a surface/volume ratio of 6.7 cm.$^{-1}$, and a volume of 75.3 cc. The smaller was 410 cm. long with a bore of 2.4 mm., surface/volume ratio of 16.7 cm.$^{-1}$, and a volume of 18.6 cc. Each reaction tube terminated in a three-way stopcock. The reaction tube was immersed in a thermostated bath of heavy lubricating oil, the temperature of which was controlled by a vapor pressure type regulator to 0.05°.

The first element in the analytical train was an ice-cooled bubbler containing an ethyl ether solution of purified *p*-toluidine. This substance reacts with isopropyl chlorocarbonate to form ether soluble N-*p*-tolylisopropyl carbamate and ether insoluble *p*-toluidine hydrochloride. Hydrogen chloride in the product mixture also reacts with toluidine to form the hydrochloride.

After completing a run, the contents and washings of the bubbler were transferred to a beaker, and an excess of dilute nitric acid added, so that the unreacted toluidine was taken into the water phase. The ether was evaporated by means of a radiant heat lamp and an air jet. The crystalline residue of N-*p*-tolylisopropyl carbamate remaining on the water was collected on a fritted glass crucible, dried under vacuum, and weighed. The quantity of carbamate served as a measure of the unreacted chlorocarbonate in the product stream.

Silver nitrate was added to the filtrate from this operation, and the silver chloride precipitate filtered, dried, and weighed. This served as a measure of the chlorine obtained from both unreacted chlorocarbonate, and free hydrogen chloride in the reaction products, so that the quantity of free hydrogen chloride could be calculated.

Following the bubbler was an anhydrone absorption tube, and a conventional ascarite tube for the determination of carbon dioxide. The analytical system was completed by a soda lime guard tube.

The vapor pressure of isopropyl chlorocarbonate was determined by operating the above system without heating the reactor, following the familiar "gas saturation" method of determining vapor pressures. The following equation expresses the vapor pressure of isopropyl chlorocarbonate as a function of temperature

$$\log_{10} P = 8.128 - 1976/T$$

Pressures are expressed as mm. and temperatures as °K.

Before beginning a decomposition rate determination, the thermostat was brought to reaction temperature, and the chlorocarbonate bubbler temperature was set. Steady nitrogen flow was then maintained through the system for more than an hour, with the reaction products being vented through the three-way stopcock into the water arm. In this way a steady state of decomposition was attained before any measurements were made. Following this period, the product stream was diverted through the analytical system for a timed interval, usually several hours.

The results of runs made in this fashion at 180, 200 and 220° are given in Table II.

Discussion of Results

Since careful observations indicated that carbon dioxide, isopropyl chloride, propylene and hydrogen chloride were the only products of the decomposition, it was evident that two reactions were occurring, the end-products of which were (1) isopropyl chloride and carbon dioxide, and (2) propylene, hydrogen chloride and carbon dioxide.

The static rate experiments showed final pressures between 2.45 and 2.52 times the initial pressure, thus indicating hydrogen chloride production to proceed to the extent of 45–52% of the total decomposition. As is shown in Table II, the flow experiments, in which reaction times were far shorter, gave hydrogen chloride production of 38–71% of total decomposition, averaging 52%. It is thus evident that the proportionate quantity of hydrogen chloride in the decomposition products does not change significantly during the course of

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(10) L. F. Fieser, THIS JOURNAL, **46**, 2639 (1924).

TABLE II

RATE OF ISOPROPYL CHLOROCARBONATE DECOMPOSITION: FLOW EXPERIMENTS

Expt. no. and cell[a]	No. of runs	Temp., °C.		Initial concn.[b] $10^4 \times$ mole/l.	Flow rate,[c] cc./sec.	Fraction decomposed	HCl ratio[d]	Rate constants			
								First order $10^4 \times$ sec.$^{-1}$			Second order l./mole sec.
								Over-all	HCl reaction	Isopropyl chloride reaction	Over-all
1-L	2	180.0	Avg.	6.3	0.30	0.20	0.41	8.5	3.5	5.0	1.35
			Range	5.83–6.76	0.23–0.37	0.15–0.24	0.38–0.44	8.1–8.9	3.4–3.6	4.5–5.5	1.3–1.4
2-L	7	180.0	Avg.	2.30	0.38	0.16	0.60	9.3	5.8	4.0	4.3
			Range	..	0.38–0.39	0.13–0.19	0.45–0.68	8.3–11.0	5.0–6.4	3.1–6.0	3.6–5.0
1 and 2	9	180.0	Avg.	..	..	..	0.54	9.1	5.0	4.3	3.6
Average			P. E.[e]	..	..	..	0.05	0.2	0.4	0.3	0.5
3-L	5	200.0	Avg.	3.01	0.43	0.47	..	37	...	...	17
			Range	..	0.41–0.47	0.45–0.52	..	35–41	...	...	16–20
4-S	7	200.0	Avg.	3.01	0.44	0.11	..	29	...	...	9.6
			Range	..	0.38–0.47	0.07–0.16	..	16–44	...	...	5.3–15.0
3 and 4	12	200.0	Avg.	3.01	..	..	..	32	...	...	..
Average			P. E.	..	..	..	..	3	...	...	..
5-L	8	220.0	Avg.	2.37	3.0	0.23	0.52	98	51	47	47
			Range	..	2.26–3.52	0.19–0.25	0.38–0.71	80–114	41–74	28–69	38–56
			P. E.	..	..	..	0.04	4	3	4	2

[a] L, Large cell: 6.0 mm. bore Pyrex, 270 cm. long: volume 75.3 cc., surface/volume 6.7 cm.$^{-1}$; S, Small cell: 2.4 mm. bore Pyrex, 410 cm. long: volume 18.6 cc., surface/volume 16.7 cm.$^{-1}$. [b] Isopropyl chlorocarbonate in pure nitrogen gas. [c] Gross input flow rate under reaction conditions. Total reaction pressure approx. 780 mm. [d] Moles hydrogen chloride in products/total moles chlorocarbonate decomposed. [e] Probable error of the mean, plus or minus.

the decomposition. This view is supported by the static rate experiments: the pressure functions described above will plot a straight line *versus* time only when the ratio of products is independent of time; and such straight lines were observed.

Reaction rates in the flow experiments were calculated under the assumptions that diffusion effects were negligible and that reaction time was given by cell volume divided by volumetric input rate. Heat transfer calculations indicated that the entering gas reached reaction temperature before a significant part of its time of passage through the cell had elapsed. It is realized that the more elaborate rate equations of Benton[11] and Hulbert[12] are proper here, but their correction is not significant when the reactant is a very small fraction of the total flowing gas, as was the case in these experiments.

The order of the reaction is indicated by a comparison of first and second order constants calculated at 180°. The value of the first order constant is independent of the concentration as indicated by a comparison of Experiments 1-L and 2-L. Second order constants show a direct dependence on concentration, thus confirming the first order behavior of the reaction. The static rate constants also show a first order behavior.

In order to test the homogeneity of the reaction two reactors were used at 200°, so that the surface/volume ratio was varied. In Experiment 3-L, where surface/volume was 6.7 cm.$^{-1}$, the average rate at 200° was 37 $\times$ 10^{-4} sec.$^{-1}$. In Experiment 4-S, where surface/volume was 16.7 cm.$^{-1}$, the average rate dropped to 29 $\times$ 10^{-4} sec.$^{-1}$. Lowering of reaction rate as surface increases is normally interpreted as being due to breaking long reaction chains on the walls. This, however, is not expected from reactions of the type here considered. Furthermore the discrepancy between the two averages is not abnormal, and is much less than would be expected for definite wall effects. One is forced to conclude that the reaction is essentially homogeneous. Apparently the reaction becomes homogeneous when the reactor walls are coated with decomposition products, and this coating is protected from atmosphere contact between runs. These views are substantiated by other investigators.[12a]

The constants which reflect the effect of temperature on the reaction rate are given for the various reactions in Table III; they correspond to the equations[13]

$$k = ae^{-E_{\text{act}}/RT} = \frac{kT}{h}e^{S_{\text{act}}/R}\, e^{-E_{\text{act}}/RT}$$

The values and probable errors of the constants were calculated from the fundamental rate data, (whose averages are given in Table II), according to the least squares equations of Youden.[14]

The mechanism of the reaction may now be considered. The mechanism postulated must allow for the production of both hydrogen chloride and isopropyl chloride, so that at least two reactions appear to be involved.

Possible mechanisms appear to be: (1) a chain or free radical mechanism, (2) decomposition producing isopropyl chloride followed by its decomposition into propylene and hydrogen chloride, (3)

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(11) H. F. Benton, THIS JOURNAL, **53**, 2984 (1931).

(12) H. W. Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944).

(12a) D. Brearley, G. B. Kistiakowsky and C. H. Stauffer, THIS JOURNAL, **58**, 43 (1936).

(13) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 295 ff.

(14) S. J. Youden, *Anal. Chem.*, **19**, 946 (1947).

TABLE III

ENERGIES AND ENTROPIES OF ACTIVATION IN CHLOROCARBONATE

	Frequency factor, *a*, sec.$^{-1}$	Energy of activation, $E_{\text{act.}}$, cal./mole	Entropy of activation, $S_{\text{act.}}$, cal./mole deg.
Isopropyl chlorocarbonate:			
Over-all decomposition	3.1×10^9	26360 ± 760	−16.1 ± 1.6
Reaction producing HCl	1.3×10^9	25760 ± 1000	−17.8 ± 2.1
Reaction producing isopropyl chloride	2.3×10^9	26430 ± 1200	−16.6 ± 2.5
Ethyl chlorocarbonate[1,2]	5.5×10^{10}	29410	−10.34

decomposition into carbon dioxide, propylene and hydrogen chloride, followed by recombination to produce isopropyl chloride or (4) simultaneous decompositions, one producing isopropyl chloride and carbon dioxide, the other producing carbon dioxide, propylene and hydrogen chloride, with negligible recombination.

Chain and free radical reactions require high activation energies, have definite wall effects, and would be expected in this case to yield a series of hydrocarbons, principally propane. However, the products of the decomposition of isopropyl chlorocarbonate appear to be limited to carbon dioxide, isopropyl chloride, propylene and hydrogen chloride. Furthermore, the activation energy is low, and no significant wall effects were observed. In view of these considerations the reaction is not believed to follow a chain mechanism.

The second possible mechanism to be considered requires decomposition of the chlorocarbonate into carbon dioxide and isopropyl chloride, the isopropyl chloride subsequently decomposing into hydrogen chloride and propylene. Lessig[4] reports the decomposition of isopropyl chloride at 335° with a half-life of eighty-five minutes. Thus the rate of isopropyl chloride decomposition, and consequently the rate of hydrogen chloride formation, would be extremely slow at 200° (half-life estimated as 6000 hours), and negligible quantities of hydrogen chloride would be formed during reaction times of the order of several hours. This conclusion does not agree with the observation that hydrogen chloride is produced in a relatively fixed ratio of about 52% of total decomposition throughout the course of the reaction, where reaction times ranged from several minutes to several hours. Therefore this mechanism is not feasible.

The recombination of propylene and hydrogen chloride postulated by the third mechanism must be quite rapid, and equilibrium reached promptly, if the ratio of hydrogen chloride to total decomposition is to be constant at a value of about 52% throughout the course of the reaction. But the value of 52% indicates that approximately equal quantities of hydrogen chloride, propylene and isopropyl chloride would be present at equilibrium. Since at equilibrium the rate of production and decomposition of isopropyl chloride must be equal, it follows that the rate of decomposition of isopropyl chloride according to this hypothesis would be very rapid at 200°. This contradicts the conclusions drawn while considering the previous mechanism, and thereby invalidates this third mechanism.

The mechanism which postulates two simultaneous decompositions is in agreement with all observed facts, and no objections to it have been found. It is believed that this path is followed. Before considering the details of the mechanism, several observations are of interest.

Dipole moment studies by Choppin and Wood[15] on several chlorocarbonates including the ethyl and isopropyl compounds, indicate that the normal configuration of the chlorocarbonate group is that in which the chlorine approaches the alkyl group, resulting in a ring-like structure. However, rotation about the RO–(COCl) bond appears to be only partially restricted, and other configurations undoubtedly exist, particularly at higher temperatures.

A number of investigators[13,16,17,18] have postulated a ring-like structure of the activated complex of certain decomposition reactions. In these cases four-membered rings were involved and the entropies of activation ranged between −10 e.u. and −18 e.u. The lowered entropy of the activated complex results from the freezing in the transition state of several rotational degrees of freedom which were active in the unactivated molecule.

It is reasonable to believe that the decomposition of ethyl chlorocarbonate begins with the formation of a ring-like activated complex, as the chlorine atom approaches the alpha alkyl carbon. Continuation of this approach permits the formation of an alkyl carbon–chlorine bond, accompanied by simultaneous ejection of carbon dioxide. The entropy change involved in the ring formation is the entropy of activation, −10 e.u., and the energy of activation is 29 kcal.

In the isopropyl chlorocarbonate decomposition, the situation is more complex. It is evident that the introduction of the second methyl group on the α-carbon has resulted in an additional reaction, producing hydrogen chloride, as well as the expected reaction yielding isopropyl chloride. Any acceptable postulate must account for this behavior.

It is probable that the constants of the decomposition reaction producing isopropyl chloride are approximately equal to those of the ethyl compound, and the mechanism of the process the same. Since the constants of the ethyl reaction are somewhat different from those observed for the isopropyl decomposition, it is probable that a com-

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(15) R. E. Wood, Ph.D. Dissertation, Louisiana State University, 1942.

(16) F. Daniels, *Ind. Eng. Chem.*, **35**, 504 (1943).

(17) O. K. Rice and H. Gershinowitz, *J. Chem. Phys.*, **3**, 479 (1935).

(18) C. C. Coffin, *Can. J. Research*, **5**, 636 (1931); **6**, 417 (1932).

pensating variance occurs in the constants of the second reaction. The entropy of activation of the reaction producing hydrogen chloride is thus thought to be about −20 e.u., and the energy of activation around 23 kcal. The more negative entropy of activation of this reaction is consistent with the view that the process is also one of internal rearrangement, involving a six-membered ring rather than a four-membered one. Examination of possible configurations by means of Fisher-Hirshfelder atomic models has suggested that the activated complex of the reaction producing hydrogen chloride is a configuration in which the chlorine atom lies between the two methyl groups of the isopropyl radical. This configuration is obviously impossible for the ethyl compound, and probably accounts for the difference in the behavior of the two chlorocarbonates.

In the case of the isopropyl compound the position of the chlorine atom allows the formation of six-membered rings, involving the methyl hydrogen and carbon atoms. The chlorine attack occurs on one of the hydrogens attached to a methyl group, and hydrogen chloride is formed. The remainder of the molecule being unstable, rearrangement occurs, forming propylene and carbon dioxide. By this mechanism no side reactions are to be expected. Furthermore, the formation of an activated complex containing a six-membered ring would freeze more degrees of freedom than the four-membered ring, and so a more negative entropy of activation is to be expected.

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Summary

Isopropyl chlorocarbonate has been found to decompose in the range 180–220°. The decomposition is homogeneous and first order, following the equation $k = 3.1 \times 10^9 e^{-26360/RT}$. Two simultaneous decomposition reactions occur, one producing isopropyl chloride and carbon dioxide, and the other producing propylene, hydrogen chloride and carbon dioxide. Mechanisms of internal rearrangement are proposed.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF DUKE UNIVERSITY]

Vapor Pressures of Trimethylbenzenes in the Low Pressure Region[1,2]

BY E. R. HOPKE AND G. W. SEARS

The vapor pressures of the isomeric trimethylbenzenes have been reported in the region 10–750 mm. A study of the ultraviolet absorption spectra of these compounds in the vapor, which is in progress in this Laboratory, made it desirable to have vapor pressure data available in the region 0.01–1.0 mm. The measurements were made with a Rodebush manometer.

Compounds.—These samples of API–NBS hydrocarbons have been made available through 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 direction of Frederick D. Rossini, from material supplied by the following laboratories: mesitylene and hemimellitene, by the A.P.I. Research Project 45 on the "Synthesis, and properties of hydrocarbons of low molecular weight" at the Ohio State University under the supervision of Cecil E. Boord, pseudocumene, by the A.P.I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons" at the National Bureau of Standards under the supervision of Frederick D. Rossini. The mesitylene (1,3,5-trimethylbenzene) was stated to contain 0.04 ± 0.02 mole % impurities; the pseudocumene (1,2,4-trimethylbenzene) was stated to contain 0.32 ± 0.20 mole % impurities; and the hemimellitene (1,2,3-trimethylbenzene) was stated to contain 0.010 ± 0.009 mole % impurities.

Experimental

The vapor pressure measurements were made with a Rodebush gage of the type described by Rodebush and Henry.[3] The calibration of the gage has been previously described by Sears and Hopke.[4]

A 0.5-ml. sample of the compound under investigation was vacuum distilled into an outgassed break-seal vessel. This vessel was sealed on to the vapor enclosure via a seal-off constriction. After the gage had been evacuated to 10^{-6} mm. accompanied by torching, the break-seal was broken and the compound was distilled into the vapor enclosure. The sample was frozen out with Dry Ice and the empty break-seal vessel was sealed off from the gage.

The sample was then melted and refrozen with Dry Ice with the vapor enclosure closed off from the vacuum pumps. The enclosure was then opened to the vacuum and the evolved gases were removed by a ten-minute pump-out period. The outgassing procedure was carried out four times in all.

An attempt to measure the vapor pressure of the sample following this outgassing procedure was abandoned when it was found that the sample continued to evolve a volatile substance. Since the gage contained, beside the com-

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(1) This investigation was assisted by the Office of Naval Research under contract N6Ori-107, Task Order I, with Duke University.

(2) Taken from part of a thesis submitted by E. R. Hopke in partial fulfillment of the requirements for the degree of Master of Science at Duke University.

(3) Rodebush and Henry, THIS JOURNAL, **52**, 3159 (1930).

(4) Sears and Hopke, *J. Phys. Chem.*, **52**, 1137 (1948).