has been recommended as a catalyzer for the oxidation of ammonia by Wortmann.

5. The example of silver taken as a catalyzer which does not form oxides and does not change its metallic individuality with rise of temperature demonstrated that near the fusing point the catalytic activity falls abruptly simultaneously with a change of the type of the reaction itself at the fusing point.

6. From this it becomes likely that in the process of decomposition of methyl alcohol by zinc the nature of the increasing activity may be explained by the formation of zinc oxide similarly to what had been demonstrated by us in the case of oxidation of ammonia by fused tin, where the increasing activity is related to the formation of tin oxide.

7. The formation of tin oxide in the process of decomposition of methyl alcohol is very probable, as Bone and Davies have demonstrated that its thermal decomposition takes place according to the equation $CH_3OH \longrightarrow CH_4 + O$, and the reaction takes place according to the equation $2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$.

The formation of zinc oxide in proportion to water vapor is also quite evident, as in the case of $CH_3OCH_3 \longrightarrow C_2H_6 + O$; the formation of zinc oxide is inevitable.

8. The attempted decomposition of methyl alcohol vapor by zinc chips at 360–400° undertaken by us showed experimentally that zinc chips either are partially covered by zinc oxide on their surface or go over to it completely, depending on the quantity of methyl alcohol that has been passed and the time this has taken.

9. From the aforesaid, it is to be acknowledged that the conclusion of Steacie and Elkin that the surface of zinc is equally active and that in general the catalytic activity of a solid matter cannot be ascribed to a limited part of its surface, is baseless and results from an insufficient cleanness of the experiment.

CHARKOW, RUSSIA RECEIVED MARCH 15, 1935

NOTES

Thermocouples from 2 to 90° Absolute

BY J. ELSTON AHLBERG AND WALTER O. LUNDBERG

In the establishment of temperature scales, several methods are being employed. Due to the necessity of setting up an accurate temperature scale between 20 and 70°K. it was thought desirable to test mathematical equations relating the electromotive force of thermocouples to temperature. The general trend of the data given by Giauque and associates[1,2] for a copper–constantan thermocouple (ice reference junction) between 13 and 90° K. made it apparent that the following simple equation might accurately represent the results

$$E = A + BT^2 + CT^3 + DT^4$$

E is the thermocouple voltage in microvolts, T is the absolute temperature, A, B, C and D are constants. The third law of thermodynamics requires that the term associated with the first power of temperature be equal to zero. Terms associated with powers of temperature higher than the fourth are assumed negligible.

Using the values by Giauque and associates[1,2] at 15, 20, 70 and 90°K. we find $A = 6681.26$, $B = -1.6547 \times 10^{-1}$, $C = 5.5460 \times 10^{-4}$ and $D = -9.878 \times 10^{-7}$. The agreement between the data of Giauque and associates and the above equation is as follows: from 13 to 23°K. better than 0.008°; from 24 to 35°K. better than 0.05°; and from 40 to 90°K. better than 0.03°. The agreements are well within the limits of accuracy claimed by them. The agreements additionally indicate the validity of the temperature scale at the University of California and of the data used in its establishment.[3] Moreover, the average deviation of the temperature coefficients of voltage from the calculated values is but 0.3%.

At the Johns Hopkins University we have experimentally compared a copper–constantan ther-

---

(1) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

(2) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

(3) Onnes, Keesom and Associates, *Comm. Phys. Lab. Univ. Leiden*; Simon and Lange, *Z. Physik*, **15**, 312 (1923).

mocouple (ice reference junction) with a helium gas thermometer between 2 and 20°K. and with oxygen vapor pressures between 70 and 90°K. The average deviation of the thermocouple voltages from the above equation is less than 0.01%. The constants determined are $A = 6039.9$, $B = -1.5475 \times 10^{-1}$, $C = 6.2064 \times 10^{-4}$ and $D = -1.5652 \times 10^{-6}$.

Comparisons of the above sets of experimental data, and of other thermocouples, show, to a first approximation, that the differences in voltages of two different thermocouples are proportional to their average voltage. The limitations of this last rule can be estimated from the two sets of constants given in this report.

The data discussed suggest that only four isolated comparisons of voltage and temperature are necessary in the calibration of thermocouples for use below 90°K.[4] However, when time and equipment are available, direct experimental calibration of thermocouples is to be preferred to the method suggested in this report.

(4) At temperatures lower than 20°K. the temperature coefficient of voltage of thermocouples becomes very small making it advisable to resort to other methods for temperature measurement.

CHEMICAL LABORATORY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

RECEIVED JULY 16, 1935

The Thermal Reaction between Gaseous Iodine Monochloride and Hydrogen

BY W. D. BONNER, W. L. GORE AND DON M. YOST

It has been found that at about 200° and above, gaseous iodine monochloride and hydrogen react slowly to form hydrogen chloride and iodine. That no hydrogen iodide is present in the reacting mixture is shown by the results of some unpublished experiments made by the late Prof. H. P. Ramsperger, who found that iodine monochloride and hydrogen iodide react very rapidly to form iodine and hydrogen chloride. A simple free energy calculation shows that this reaction goes practically to completion. The main reaction between iodine monochloride and hydrogen is then

$$2ICl(g) + H_2(g) = I_2(g) + 2HCl(g)$$

Inasmuch as no pressure change accompanies the reaction, the compositions of the reacting mixtures were determined iodimetrically. Weighed quantities of best quality liquid chlorine and solid iodine in small breakable capsules were placed in 100-cc. bulbs. The bulbs were evacuated and then filled to the desired pressure with hydrogen which had been carefully freed from oxygen and water vapor. After sealing off, the bulbs were shaken to break the capsules and were then immersed in a thermostat filled with molten Crisco. At suitable time intervals a bulb was removed from the thermostat, and the reaction was stopped by cooling the bulb rapidly in an air blast. Independent experiments had shown that no detectable reaction takes place below 100°. The cooled bulbs were opened under a solution of potassium iodide and the resulting iodine titrated with 0.1 N thiosulfate.

The best constants were obtained when the rate equation was assumed to be

$$-d(ICl)/dt = k(H_2)(ICl)$$
$$k = \frac{2 \times 2.303}{t(c_1 - 2c_2)} \log \frac{2c_2(1 - B)}{2c_2 - c_1B}$$

where c_1 and c_2 are the initial concentrations of $ICl(g)$ and $H_2(g)$, respectively, and B is the fraction of ICl consumed in time t. At 205°, $k = 0.031 \pm 0.006$; at 230°, $k = 0.17 \pm 0.06$; and at 240°, $k = 0.35 \pm 0.06$. The concentrations of ICl and H_2 are here expressed in moles per liter, and the time is given in minutes. Experiments in which the bulbs were filled with powdered Pyrex glass yielded, within the errors indicated, the same values for the specific rate constants. Representative results of the experiments are presented in Table I.

TABLE I

RESULTS OF REACTION RATE EXPERIMENTS

Temp., °C.	t, min.	Moles per liter $c_1 \times 10^2$	$c_2 \times 10^2$	Fraction ICl reacted B	k
205	360	3.12	3.19	0.329	0.033
	360	4.43	3.19	.199	.021
	60	2.20	3.15	.0674	.038
230	120	3.09	3.42	.402	.139
	60	2.53	3.43	.376	.248
	60	2.04	3.43	.202	.113
	31	1.49	3.43	.131	.138
	31	2.66	3.45	.113	.116
	30	2.68	3.13	.155	.180
	15	2.24	3.43	.098	.208
240	85	2.41	3.44	.466	.322
	50	1.38	1.94	.241	.298
	48	2.13	2.73	.375	.414
	39	1.68	1.94	.188	.284
	31	1.62	3.44	.350	.420

The mechanism suggested by these results is the following, which is put forward as a purely tentative one

$$H_2 + ICl = HI + HCl \qquad \text{(slow)}$$
$$HI + ICl = HCl + I_2 \qquad \text{(rapid)}$$

The deviation of the values of individual rate constants from the mean is appreciably greater than is usually found where a single mixture can be followed with time, yet no correlation between the deviations and the concentrations of reactants or products is evident.

It must be pointed out that iodine monochloride dissociates[1] somewhat (3% at 210°) into iodine and chlorine, and that a mechanism involving the possible reaction of hydrogen with chlorine must be considered. Inasmuch as the dissociation is greatly repressed as soon as some free iodine is formed, and since mixtures initially containing excess iodine gave sensibly the same results, such a mechanism does not seem likely. The direct reaction between hydrogen and iodine is very slow at 240° and below.[2]

When the average values of the specific reaction rate constants are plotted against $1/T$ a straight line results. The energy of activation for the assumed slow reaction is 33,900 cal.

---

[1] McMorris and Yost, THIS JOURNAL, **54**, 2247 (1932).

[2] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

CONTRIBUTION FROM
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 484
AND FROM THE CHEMICAL LABORATORIES
UNIVERSITY OF UTAH, NO. 46

RECEIVED JUNE 25, 1935

Specific Heat and Binding Conditions of Adsorbed Argon on Charcoal

BY HANS M. CASSEL

When a monoatomic gas is adsorbed at the surface of an elementary solid, the first adsorption layer represents a more or less perfect continuation of the crystal lattice. Accordingly, the "adatoms"[1] behave as being bound by certain centers of attraction around which they move similarly as the atoms of the adsorbent. But, due to the anisotropy of the situation, the oscillation perpendicular to the surface freezes in, if the temperature is enough decreased, whereas the degrees of freedom parallel to the surface, corresponding to weaker binding forces, remain still excited at much lower temperatures.

It depends on the size and shape of the potential box in which the adatom may be regarded as contained,[2] whether the movement is a two-dimensional translation or a two-dimensional harmonic oscillation. Accordingly, the specific heat of the adatoms, in the first case, has the value, R, remaining constant except at extremely low temperatures, and, in the second case, the value, $2R$, decreasing with decreasing temperature in analogy to the Debye function of the three-dimensional oscillator.

F. Simon and R. C. Swain[3] recently having measured the heat capacity of argon adsorbed on charcoal observed the rather constant value, R, between 80 and 60°K., but, at lower temperatures, a decrease leading to an almost imperceptible amount below 20°K. Thus, the experimental result agrees neither with the first nor with the second possibility explained above. Instead, the appearance of the sloping-down perfectly resembles the Debye function of a one-dimensional oscillator.

This view, indeed, is justified, since it is much more probable that an argon atom is adsorbed in the hollow edges or steps of the very cleavable material than on the smooth surfaces of the netplanes. Adatoms bound by two vicinal crystal planes, at low temperatures, are capable of only one-dimensional vibrations parallel to both surfaces. The specific heat measurements, therefore, back the suggestion that the majority of the argon atoms is adsorbed in this way.

---

[1] I. Langmuir, *J. Chem. Physics*, **1**, 3 (1933).

[2] The author is very much indebted to Dr. L. Pauling, Cal, Tech., for the calculation of the degeneracy temperature.

[3] F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

STANFORD UNIVERSITY
STANFORD UNIV., CALIF. RECEIVED SEPTEMBER 3, 1935

Areametric Analysis. A Useful Technique in Estimating Small Amounts of Heavy Precipitates

BY V. R. DAMERELL AND M. AXELROD

In attempting to measure small amounts (0.01 to 5 mg.) of lead sulfate in contact with sulfuric acid, the authors were able to develop a simple technique whereby compact circular (or square) piles of precipitate could be obtained, of reproducible dimensions, in the center of the flask bottom (see Fig. 1). The apparent areas of these "spots" (as viewed from above, and assuming them to be flat circles or squares) could be readily measured and compared to the areas produced by known amounts of precipitate. This method of analysis is new, according to the authors' best knowledge, and since it involves the measurement of an area, the term areametric analysis is proposed.

The method is generally applicable to heavy precipitates of the lead sulfate type, such as barium sulfate, lead arsenate, lead chromate, etc. The determination is made right in the precipitation beaker or flask, and the procedure is of such simplicity that the authors feel the method may be of considerable use in the estimation of small amounts of many substances.

The technique used in the formation of these "spots" was as follows. The liquid in the flask was first swirled twenty or thirty times, to loosen the precipitate and cause part of it to go to the center. Then after allowing the precipitate to settle for a minute or two, the flask was tipped so that the line made by the edge of the liquid crept nearly to the center of the flask bottom. Sufficient liquid was present in the flask so that the flask bottom made a maximum angle of about 60° with the desk top. This was done ten times to the left, ten times to the right, and ten times each backward and forward. The precipitate was brought to the center of the flask bottom by this procedure.

Finally the flask was held by the thumb and finger of the right hand near the bottom and the thumb and finger of the left hand near the top, over a black surface. The right hand now made a series of short backward and forward movements (about ten to a series, at the rate of three or four a second). During these movements the flask did not move more than a millimeter or two, and the force was applied by the whole forearm, the wrist being held practically stiff. After each series of shakes the flask was rotated 30 or 40°. These vibrational movements caused the precipitate to be swept into a compact circular pile. Photographs of spots obtained are given in Fig. 1. After a few minutes of such shaking the spot reached an essentially constant, minimum size. The flask was then placed on the "standard spot" card (Fig. 2) and moved along until a spot was reached which matched the unknown spot in size. This card was simply a reduced copy of a contact photograph of a twist drill and steel wire gage. It was calibrated with known amounts of precipitate. A sheet of millimeter graph paper can be substituted for occasional determinations.

Fig. 1.—Lead sulfate "spots."

This vibration method was used to obtain circles having an apparent area up to about twenty square millimeters. For larger amounts than this the minimum area of the square was obtained by the tipping process described above. The dimensions of the square could be rapidly obtained by placing the flask on millimeter graph paper.

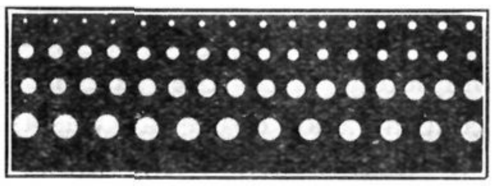

Fig. 2.

Quantitative results are given in Table I for lead sulfate in contact with 10 cc. of 40% sulfuric acid, measured in a 50-cc. Pyrex Erlenmeyer flask.

TABLE I

Mg. lead present	Mg. lead found	Impurities present, mg.	Mg. lead present	Mg. lead found	Impurities present, mg.
0.08	0.08	None	0.06	0.08	Sn (10)
.20	.19	None	.10	.13[a]	As (10) Bi (1)
.13	.14	None	.20	.19[a]	Cu (10) Cd (1)
.10	.09	None	.30	.32[a]	As (1) Bi (1) Cu (1)
.04	.06	None			Sb (1) Sn (1)
.02	.03	None	.40	.37[a]	Cu (1) Cd (1)
.04	.05	None	.50	.54[a]	Cu (10) Cd (10)
.20	.15	Cd (10)	1.0	1.3[a]	As (10) Bi (10)
.12	.10	Cu (50)			Cu (10)
.09	.10	Bi (10)	2.0	1.8[a]	Cu (5) Cd (5)
.08	.08	Bi (50)	3.0	2.7[a]	As (5) Sb (10)
.06	.12	As (50)			Sn (10)
.17	.18	Sb (10)	4.0	4.2[a]	Cu (4) Cd (4)

[a] Precipitate washed three times, redissolved and reprecipitated.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO

RECEIVED SEPTEMBER 3, 1935

The Catalytic Oxidation of Carbon

BY JESSE E. DAY,[1] RICHARD F. ROBEY AND HYP J. DAUBEN

A few years ago, Taylor[2] reported a means of demonstrating the peculiar catalytic effect of sodium chloride on the oxidation of soot carbon, a phenomenon well known to the layman in its practical application.

We have successfully performed the demonstration of Taylor many times; it was discovered, however, that not only sodium chloride is effec-

---

(1) Because of the untimely death of Professor Jesse E. Day, on April 19, 1935, the junior authors have been deprived of the benefits of his kindly guidance and criticism in the preparation of this paper.—R. F. R. and H. J. D.

(2) R. K. Taylor, THIS JOURNAL, **52**, 3025 (1930).

tive, but other salts apparently equally as well. This seemed so striking that we immediately endeavored to verify this observation in a somewhat more exact manner.

A small tube (2.4 cm. in diameter) was rotated (3 r. p. m.) on its long axis inside a split type laboratory combustion furnace. A short (4 cm.) length of the tube, in the center of the furnace, and having a negligible temperature gradient, was coated completely with the salt in question. Thus the concentration of the salt was assumed to be constant at the carbon–salt interface. The temperature of the furnace was then increased to and maintained at a predetermined convenient value (±3°). Carbon film deposition, mirror reflected observation, and air admittance were made through a narrow longitudinal slot (2 cm. wide) in the under portion of the surrounding furnace. The apparatus was entirely enclosed in a small glass-fronted cabinet to protect it from drafts.

Carbon deposition was carried out by means of a wide flame of enriched natural gas from a Pyrex glass burner which moved mechanically along the slot in the furnace at a uniform rate (0.02 cm./sec.). The flame deposited the carbon film uniformly, as evidenced by the manner in which it disappeared on oxidation, and at a rate of 3.5 micromoles/sec., reproducible within 10%.

The lengths of time required for the disappearance of the carbon film from the 4 cm. sector were determined when deposited on bare glass as well as on the following C. P. salts: lithium, sodium, potassium, calcium, strontium and barium chlorides, calcium and barium hydroxides, sodium and potassium sulfates.

At 575° the carbon burned off the bare glass in about 180 sec. This was cut down by all of the salts to between 20 and 30 sec., as far as could be discerned by the method of observation. At 550° the oxidation of the carbon from the bare surface required 280 sec. It was reduced by the presence of the salts to 130–150 sec. At 515°, the oxidation from the bare surface required 630 sec. This was cut down by the barium and strontium salts to about 300, by the calcium salts and sodium chloride to about 230, and by the potassium and lithium chlorides, and sodium and potassium sulfates to about 170 sec. The values given are the averages of two or more observations usually agreeing within 10% or less. This agreement evidences a fair reproducibility of oxidizable surface area.

The most ready explanation of the effect of salts in the oxidation of carbon is that offered by Taylor and Neville.[3] They pointed out that the probable function of salts in the reaction of steam on carbon is in hastening the decomposition of the C_xO_y surface complex. With this barrier removed, a carbon surface is more readily attacked by oxidizing gases.

[3] H. S. Taylor and H. A. Neville, THIS JOURNAL, **43**, 2055 (1921).

CHEMICAL LABORATORY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

RECEIVED AUGUST 5, 1935

The Isolation and Identification of a Paraffin Hydrocarbon from Urine of Pregnancy

BY WILLIAM FORRIS HART AND M. ALLEN NORTHUP

Marrian[1] has mentioned that a paraffin hydrocarbon which is physiologically inactive, occurs in urine of pregnancy. Schwenk[2] also states that he has encountered a physiologically inactive hydrocarbon in urine of pregnancy.

We have isolated and identified one hydrocarbon, heptacosane, from urine of pregnancy, and have evidence of the presence of another, pentacosane, in the same material.

Experimental.—Twelve liters of urine were aged for several months and acidified to Congo red with concentrated hydrochloric acid, the acidified urine was then treated with 28 g. of fuller's earth per liter, agitated thoroughly, and allowed to stand overnight. The fuller's earth was then filtered off, and a second absorption on 14 g. per liter was applied. The combined fuller's earth fractions were air dried and extracted seven times with convenient volumes of low boiling petroleum ether (below 70°). The combined petroleum ether residue was taken up in 50 cc. of ethyl acetate. This solution, on chilling, deposited 1.4 g. of white plate-like crystals. It was found on recrystallizing from methanol that this material could be separated into two fractions, one soluble, and the other insoluble, in warm methanol.

The fraction insoluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was 58–59° (uncorrected). Analysis gave: C, 85.83 and 84.56, H, 14.62 and 14.62; molecular weight (micro Rast), 391, 391. Calcd. for heptacosane ($C_{27}H_{56}$): C, 85.16,

[1] Marrian, *Physiol. Rev.*, **13**, 185 (1933).

[2] E. Schwenk, private communication.

H, 14.83; molecular weight, 380; melting point, 59°.[3]

The fraction soluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was 52–54° (uncorrected). Analysis gave: C, 85.07; H, 15.08%. Calcd. for pentacosane ($C_{25}H_{52}$): C, 85.37; H, 14.63; melting point, 54°.[3]

It is not certain whether this fraction consists of a pure hydrocarbon, or a mixture of two or more hydrocarbons. On crystallizing from ethyl acetate on a microscope slide it has the form of homogeneous hexagonal plates.

Besides the solubilities mentioned above, these fractions are very soluble in chloroform and benzene, soluble in hot and insoluble in cold acetone and ethanol, and insoluble in water and alkali.

They contain no nitrogen or phosphorus, have no acid or saponification number, do not reduce Fehling's solution, and do not absorb bromine from chloroform solution. They have been found to have no oestrogenic activity.

The procedure outlined above was applied to eight liters of non-pregnant female urine which had been aged for two weeks. From the petroleum ether was obtained 3.8 mg. of an impure waxy substance from which it was not possible to isolate any crystalline material melting below 120°.

The same procedure was also applied to two samples of male urine of eight liters each. One of these was a year old; the other had been aged two weeks. Like the non-pregnant female urine each yielded a few milligrams of impure waxy substance from which no crystalline material melting below 120° could be isolated. If these hydrocarbons occur in non-pregnant female, and male, urine they must do so in an amount far less than in urine of pregnancy. The physiological source of these hydrocarbons during pregnancy raises many interesting speculations.

The authors regret that factors beyond their control have prevented an extension of this investigation. They wish to thank Dr. F. R. Eldred, Director of Research, of Reed and Carnrick, for his kind permission to publish this work, and Dr. J. B. Niederl of Washington Square College, New York University, for the micro analyses and molecular weight determinations.

---

[3] Hildebrand and Wachter, THIS JOURNAL, **51**, 2487 (1929).

A CONTRIBUTION FROM THE
LABORATORIES OF REED AND CARNRICK
JERSEY CITY, N. J.
RECEIVED OCTOBER 25, 1935

Preparation of Alpha-Naphthoic Acid

BY D. J. LODER[1] AND F. C. WHITMORE

During some work which demanded the preparation of a considerable amount of pure alpha-naphthoic acid, all of the regular methods of preparing this substance were tried with only mediocre success. At the same time some studies were being carried out on the preparation of tertiary alcohols by the action of the Grignard reagent with diethyl carbonate and it had been observed that when the Grignard reagent was "sterically hindered" the reaction could be stopped at the ketone stage or even at the ester stage. Consequently, alpha-naphthylmagnesium bromide (5 moles in 2.5 liters of absolute ether) was added slowly to a solution of ethyl carbonate (7.5 moles in 500 cc. of dry ether). Treatment of the mixture with a slight excess of 30% sulfuric acid, separation of the ether layer and isolation in the usual way gave a 70% yield of redistilled ethyl alpha-naphthoate boiling at 143–144.5° at 3 mm. Hydrolysis of the ester gave over a 90% yield of pure alpha-naphthoic acid.

[1] Present address: Ammonia Department, du Pont Experimental Station, Wilmington, Delaware.

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS AND
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
RECEIVED SEPTEMBER 12, 1935

The Mechanism of the Addition of Halogens to Ethylenic Linkages

BY RICHARD A. OGG, JR.

The addition in solution of halogens to an ethylenic linkage is assumed by Ingold[1] to proceed through the formation of an intermediate positive carbonium ion, as $RCHBr—C^+HR$, which subsequently adds a halide ion. Experiment indicates positive carbonium ions to be configuratively unstable,[2,3] and hence this mechanism would lead one to expect identical products (*i. e.*, a mixture of meso and *dl* dihalides) from *cis–trans* isomers, in contradiction to experimental fact.

Carothers[4] has proposed that addition reactions of ethylenic linkages are initiated by an internal ionization of the double bond, followed by addition of the reagent molecule at the positive end,

---

[1] C. K. Ingold, *Chem. Reviews*, **15**, 225 (1934).

[2] E. S. Wallis and F. H. Adams, THIS JOURNAL, **55**, 3838 (1933).

[3] E. Bergmann and M. Polanyi, *Naturwissenschaften*, **21**, 378 (1933).

[4] W. H. Carothers, THIS JOURNAL, **46**, 2227 (1924).

and subsequent rearrangement to the stable addition product. Such an internal ionization of double linkages, in view of the rapid racemization of positive carbonium ions, would cause a rapid *cis–trans* isomerization of ethylene derivatives even in the absence of reagents. Hence this mechanism is open to the same objection as that of Ingold, *i. e.*, in leading to identical addition products from *cis–trans* isomers. Both mechanisms infer the addition reactions in question to be uncatalyzed.

The following mechanism is suggested as more plausible. Using bromine, for example, the consecutive reactions are

$$(1)\quad Br^- + RCH{=}CHR \longrightarrow RCHBr{-}C^-HR$$

$$(2)\quad RCHBr{-}C^-HR + Br{-}Br \longrightarrow RCHBr{-}CBrHR + Br^-$$

That is, the addition is catalyzed by halide ion, and the intermediate is a carbanion. Carbanions have been shown[2] to have stable configurations, and hence stereochemically different products should result from *cis–trans* isomers. Further, explanation is afforded of the generally observed *trans* addition of halogens to ethylenic linkages. Reaction (1) is to be regarded as a substitution reaction of the halide ion with one of the electron pair bonds of the ethylenic linkage, and hence as attended by *optical inversion* of the intermediate carbon atom.[5] The carbanion thus has a *trans* configuration, and since no configuration change attends reaction (2), the final addition product should be *trans*.

Experimental evidence for the proposed mechanism is found in a number of cases in which addition or removal of halogens from an ethylenic linkage is catalyzed by halide ions. Thus Slator[6] found the decomposition of ethylene diiodide to be catalyzed by iodide ions in alcoholic solution. Obviously the addition of iodine to ethylene must be similarly catalyzed. Reaction of a 1,2-dibromo compound with iodide ions to yield the corresponding unsaturated compound is a well-known typical reaction. Halogen addition to simple ethylenic hydrocarbons in solution is ordinarily exceedingly rapid. However, the marked slowness of the addition of bromine to ethylene in rigorously purified and dried solvents[7] indicates the ordinary reaction to be catalyzed by impurities, of which halide ions appear most likely. The otherwise immeasurably slow addition of bromine to maleic and fumaric esters was found by Hanson and Williams[8] to be catalyzed by a trace of hydrogen bromide. Finally, the author has observed, using glacial acetic acid as a solvent, that the normally slow addition of bromine to maleic and fumaric acids, stilbene, cinnamic acid and tetrachloroethylene is markedly catalyzed by dissolved lithium and potassium bromides.

A very similar mechanism to the above probably obtains for addition of hydrogen halides to ethylenic linkages, step (2) being replaced by addition of a hydrogen ion to the carbanion. *Trans* addition should also occur in this case. Likewise the addition of halogens and hydrogen halides to acetylenic linkages should proceed in analogous fashion, giving *trans* addition products, as is actually observed.

It is to be emphasized that the above mechanism applies to reactions in solution, and in the dark. Gas phase addition of halogens to double bonds cannot of course be caused by ionic catalysis, and it is significant that no homogeneous reaction of gaseous ethylene with bromine or chlorine[9,10] is observed at low temperatures. In the photochemical reaction the chains are carried by free halogen atoms and the radicals RCHBr—CHR. The rapid racemization of the latter, followed by loss of halogen atoms, explains the well-known halogen-sensitized *cis–trans* isomerization of ethylene derivatives. Likewise, the photochemical reaction is to be expected to lead to a mixture of *cis* and *trans* addition products.

Cases in which marked *cis* addition of halogens occurs practically all involve the *ions* of maleic and fumaric acids.[11] Due to the Coulomb repulsion between the negative charges of the halide ion and of the acid ions, the above mechanism could hardly be expected to obtain. It is much more probable that intermediate lactone formation occurs, in which case the *cis* addition is readily explicable.

The recent communication of Anantakrishnan and Ingold[12] substantiates the above suggestion that halogen addition to ethylenic hydrocarbons is catalyzed by halide ions.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIF.
RECEIVED JULY 22, 1935

---

[5] N. Meer and M. Polanyi, *Z. physik. Chem.*, **19B**, 164 (1932); A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[6] A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

[7] H. S. Davis, THIS JOURNAL, **50**, 2769 (1928).

[8] N. W. Hanson and D. M. Williams, *J. Chem. Soc.*, 1059 (1930).

[9] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923).

[10] R. G. W. Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

[11] Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925).

[12] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 984 (1935).

Catalysis in Organic Chemistry. V. Decompositions of Esters and Acids by Anhydrous Zinc Chloride[1]

BY H. W. UNDERWOOD, JR., AND O. L. BARIL

The catalytic decomposition of esters and acids by anhydrous zinc chloride has been described in previous papers.[2] The transformations observed were represented by three different types of decomposition which involved the elimination of an aliphatic unsaturated hydrocarbon or carbon dioxide or both. In order to substantiate these results, additional experiments of a similar nature were performed, from which the following regularities and generalities may be concluded.

The methyl, ethyl, propyl and butyl esters of monobasic aliphatic acids were not affected by the catalyst under the conditions of the experiment. The esters derived from amyl alcohol and from a monobasic aliphatic acid decomposed very slowly into an unsaturated hydrocarbon and the aliphatic acid. The rate of decomposition increases with a rise in the number of carbon atoms in the alcohol group. The aliphatic monobasic acids themselves are not affected by the catalyst. Esters of aliphatic dibasic acids are all decomposed, the dibasic acid reacting with the zinc chloride to form the zinc salt of the dibasic acid with evolution of hydrogen chloride. The hydrogen chloride in turn forms the alkyl halide with the liberated unsaturated hydrocarbon.

Esters of aromatic acids decompose into an unsaturated hydrocarbon and the aromatic acid, which in turn decomposes into carbon dioxide and a saturated aromatic hydrocarbon, providing the aromatic acid is monobasic. If the aromatic acid is a dibasic acid, the anhydride of the acid is formed. Benzyl esters decompose into the acid, and the benzyl groups polymerize, forming a dark tarry residue. All unsaturated hydrocarbons evolved, whether aliphatic or aromatic, polymerize, the polymerization increasing with the rise in the number of carbon atoms in the hydrocarbon.

Esters and acids readily decomposed by heat were not used. Those which were used could be distilled or fused without decomposition. In every case, decomposition of the ester or acid was effected, in the presence of anhydrous zinc chloride, at a much lower temperature than if heated alone. Zinc chloride dissolved in the ester or acid before any evidence of decomposition appeared. Esters and acids which did not dissolve the zinc chloride on heating were not themselves decomposed. This peculiar phenomenon was also noted in the experiments described in previous papers. During the decomposition, there was always a color change from colorless to yellow to orange to red to brown and finally black. The temperature in every case was raised until the ester or acid dropped freely from the end of the reflux condenser. There was often evidence of decomposition in the reaction flask before this temperature was reached. The tests described by Mulliken ["Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, 1916, 1922, Vols. I, II and IV] were used for the identification of all the products of decomposition.

Experimental

No evidence of decomposition was found in experiments with ethyl chloroacetate, dichloroethyl acetate, trichloroethyl acetate, ethyl isovalerate, *n*-butyl formate, *n*-propyl acetate, propyl formate, isopropyl formate and methyl *m*-nitrobenzoate.

Esters Decomposing with Evolution of Carbon Dioxide.—Methyl cinnamate yielded styrene and its polymers; ethyl cyanoacetate gave ethylene and methyl cyanide; amyl chlorocarbonate decomposed into amylene and its polymers, amyl chloride and hydrogen chloride; amyl chloroacetate into amylene and its polymers, chloroacetic acid and hydrogen chloride; ethyl anisate into ethylene, anisic acid, anisole and *p*-ethyl cresyl ether; ethyl phenylacetate into ethylene, phenylacetic acid, propylbenzene and acetic acid; isoamyl valerate into valeric acid, isopropylethylene and its dimer; *n*-amyl acetate into acetic acid, amylene and its polymers; isoamyl propionate into propionic acid, isopropyl ethylene and its dimer; ethyl *m*-aminobenzoate into ethylene and aniline; and ethyl *p*-nitrobenzoate into ethylene and *p*-nitrobenzoic acid.

Ethyl acetoacetate yielded acetone, ethyl acetate and propyl methyl ketone; and isobutyl acetoacetate gave isobutylene, acetone, isobutyl acetate and methyl isoamyl ketone. Ethyl diethylmalonate gave ethylene and ethyl diethylacetate; while ethyl dipropylmalonate gave ethylene and ethyl dipropylacetate. Methyl carbonate yielded methyl alcohol; cyclohexyl acetate gave cyclohexane and acetic anhydride; while ethyl orthoformate decomposed into ethyl ether and ethyl formate when distilled over anhydrous zinc chloride, but on refluxing the mixture for one hour at 60°, ethyl alcohol and paraldehyde were obtained.

Acetal and ethylal gave ethyl alcohol and paraform, whereas dimethyl acetal yielded methyl alcohol and par-

---

[1] Due to the death of Professor Underwood, this paper has been prepared by the junior author.

[2] Underwood and Baril, THIS JOURNAL, **52**, 395 (1930); **53**, 2200 (1931).

aldehyde. Benzene was obtained from both the iso- and terephthalic acids. Anisic acid gave anisole; *p*-toluic acid yielded toluene and the zinc salt of *p*-toluic acid; and diphenylacetic acid decomposed into diphenylmethane.

Esters Decomposing without Evolution of Carbon Dioxide.—Benzyl benzoate and benzyl butyrate decomposed into their respective acids, benzoic and butyric. The benzyl groups polymerized, forming a dark colored and tarry residue. Dimethyl phthalate gave phthalic anhydride, and *n*-amyl phthalate gave phthalic anhydride, amylene and its polymers. Phenyl acetate yielded phenol; and phenyl salicylate gave phenol at a temperature of 177° in presence of the catalyst, although a temperature of 280° is required to decompose it without a catalyst. Phenylacetic acid yielded acetic acid; *m*- and *p*-nitrobenzoic acid reacted with the catalyst to form the zinc salt of the acid with evolution of hydrogen chloride. The *p*-nitrobenzoic acid mixture blew up after fifteen minutes of heating, leaving a deposit of soot over the entire apparatus.

A new type of decomposition has been observed with the elimination of carbon monoxide instead of carbon dioxide from halogenated aliphatic acids. Monochloroacetic acid decomposed into carbon monoxide, formaldehyde and hydrogen chloride; and the trichloroacetic acid decomposed into carbon monoxide, carbonyl chloride and hydrogen chloride.

The authors wish to express their thanks for a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences which partly defrayed the cost of this work.

CONTRIBUTION NO. 131 FROM THE
RESEARCH LABORATORY OF ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
RECEIVED JULY 17, 1935

Reduction of Nitroguanidine. III. Synthesis of Aminoguanidine[1]

BY G. B. L. SMITH AND EDWARD ANZELMI

Aminoguanidine has been prepared by the reduction of nitroguanidine with zinc in a solution of acetic acid,[2] by the interaction of hydrazine hydrochloride and cyanamide,[3] and by the electrolytic reduction of nitroguanidine.[4] We have prepared aminoguanidine in high purity and excellent yield by the hydrazinolysis of methyl isothiourea sulfate. To 139 g. of methyl isothiourea sulfate in 200 ml. of water at 10° is added 119 ml. of a 42% solution of hydrazine hydrate[5] diluted with an equal volume of water. The methyl mercaptan liberated can be absorbed in a solution of sodium hydroxide.[6] Finally the aminoguanidine sulfate is precipitated by addition of an equal volume of 95% ethanol to the solution concentrated to 200 ml. A second crop of crystals separates on concentration of the filtered solution. The water of crystallization (1 molecule) may be removed by drying *in vacuo* or at 105°; yield 90%; m. p. 206° with decomposition (Thiele, 207–208°). Aminoguanidine sulfate was identified through conversion to the picrate and bicarbonate, by liberation in alkaline solution of one-half of the nitrogen as ammonia and by hydrolysis to hydrazine.[7] *Anal.* calcd. for $(CH_6N_4)_2H_2SO_4$: SO_4, 39.83; NH_3, 27.67; N_2H_4, 26.02. Found: SO_4, 39.3, 39.7; NH_3, 27.2, 27.5, 27.7; N_2H_4, 26.03, 25.93. The fact that aminoguanidine bicarbonate has the composition $CN_4H_6H_2CO_3$ has been established by analysis. A solution of aminoguanidine is a strong base K_B estimated as 1.1×10^{-3}. Further work on aminoguanidine and alkylaminoguanidines is in progress.

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y.
RECEIVED MAY 3, 1935

---

[1] For more full details see B.S. thesis by Edward Anzelmi, Polytechnic Institute of Brooklyn, 1933. Contribution No. 27 from the Department of Chemistry of the Polytechnic Institute of Brooklyn.

[2] Thiele, *Ann.*, **270**, 1 (1892).

[3] Pellizzarri and Cuneo, *Gazz. chim. ital.*, [2] **21**, 405 (1901).

[4] Boehringer, German Patent 167,637. We have as yet been unable to confirm this observation.

[5] From the Eastman Kodak Company.

[6] Phillips and Clarke, THIS JOURNAL, **45**, 1755 (1923).

[7] Jamieson, *Am. J. Sci.*, [4] **33**, 353 (1912).