solved in 200 cc. of acetone was employed and after the addition of this solution the mixture was refluxed for thirty minutes and immediately filtered. The residue obtained on concentration under reduced pressure in the presence of excess cadmium carbonate was treated with absolute ethanol and the solvent removed under reduced pressure, this process being repeated several times. The sirup obtained after chloroform removal was crystallized from 70% ethanol as described by Brigl and Muehlschlegel[8] and crystallized after standing in the ice box for one week. Pure material was obtained after several recrystallizations from absolute ethanol; m. p. 81–82°; $[\alpha]^{24}_D$ +40° (*c*, 3; abs. EtOH). The constants given by Brigl and Muehlschlegel were: m. p. 76–82°; $[\alpha]_D$ +37° (EtOH).

## Summary

1. α-*d*-Galactose pentabenzoate and α-*l*-arabinose tetrabenzoate have been synthesized. New constants for β-*l*-arabinose tetrabenzoate have been reported.

2. Benzobromo-*l*-arabinose has been synthesized.

3. The benzoates of trityl-*l*-arabinose diethyl mercaptal and trityl-*d*-mannose diethyl mercaptal and the acetate of the latter have been synthesized.

4. 6-Bromo-*d*-galactose diethyl mercaptal tetrabenzoate has been synthesized.

5. The diethyl mercaptal tetrabenzoates of *d*-galactose and *d*-mannose have been synthesized through the tritylation reaction of Helferich. Hydrolysis of the ethylmercapto groups from the former produced a crystalline *d*-galactose tetrabenzoate methyl alcoholate, and from the latter an amorphous *d*-mannose tetrabenzoate.

6. Hydrolysis of the trityl and ethylmercapto groups of trityl-*l*-arabinose tribenzoate produced an *l*-arabinose tribenzoate identical with that obtained from benzobromo-*l*-arabinose. Further benzoylation of this tribenzoate produced α-*l*-arabinose-tetrabenzoate.

COLUMBUS, OHIO RECEIVED NOVEMBER 4, 1935

---

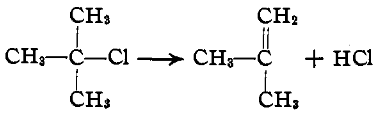
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# The Thermal Decomposition of Tertiary Butyl and Tertiary Amyl Chlorides, Gaseous Homogeneous Unimolecular Reactions

BY D. BREARLEY, G. B. KISTIAKOWSKY AND C. H. STAUFFER

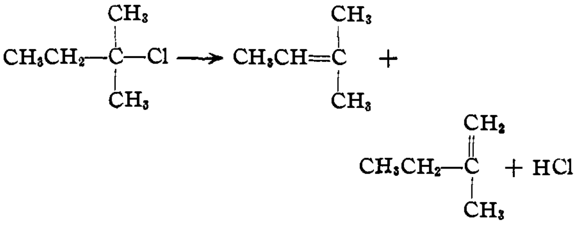
Most unimolecular reactions which have been studied[1] have the disadvantage that the decomposition is quite complex and involves the breaking down of the entire molecule or various complicated secondary reactions. It was, therefore, the purpose of this study to add to the increasing list of unimolecular reactions two more reactions involving the rupture of only two bonds, the C–H and the C–Cl bonds. Also it was for the purpose of correlating the dehydration of *t*-butyl and *t*-amyl alcohols[2] with the elimination of hydrogen chloride from *t*-butyl and *t*-amyl chlorides.

The main reactions occurring may be written as follows



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl \longrightarrow CH_3-\overset{CH_2}{\underset{CH_3}{\overset{\|}{C}}} + HCl$$

and



$$CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl \longrightarrow CH_3CH=\overset{CH_3}{\underset{CH_3}{C}} + CH_3CH_2-\overset{CH_2}{\underset{CH_3}{\overset{\|}{C}}} + HCl$$

For the study of the thermal decomposition of these tertiary chlorides a static method was used, and the *t*-butyl chloride was studied over the temperature range 547–645°K. while the *t*-amyl chloride was studied over range 543–600°K.

The previous work of Schultz and Kistiakowsky[2] on the two tertiary alcohols was also done using a static method, but in a temperature range of 760 to 830°K., so that any close similarity between these two types of reactions should indicate quite definitely the absence of any chain mechanism, and classify them as true unimolecular reactions.

---

[1] A general review of existing data, Kistiakowsky, *Chem. Rev.*, **17**, 47 (1935).

[2] Schultz and Kistiakowsky, THIS JOURNAL, **56**, 395 (1934).

## Experimental

**Preparation and Purification of Materials.**—In the preparation of the *t*-butyl chloride, the starting point was a commercial tertiary butyl alcohol from cracked petroleum hydrocarbons, and therefore was contaminated with the adjacent secondary and tertiary alcohols. This was distilled, and then fractionally crystallized six times, the first quarter to crystallize being collected each time. This was again distilled, and a freezing curve taken. The chloride was prepared from this by the method of "Organic Syntheses."[3] The *t*-butyl chloride thus prepared was then fractionally distilled, and the portion boiling from 51.0 to 51.2° was collected.

The *t*-amyl alcohol from which the *t*-amyl chloride was prepared originated from the same source as the *t*-butyl alcohol. This was fractionally distilled through a column, and the middle portion boiling at 101° collected. This was then cooled in an ice–salt mixture and allowed to crystallize slowly with stirring. The first half to crystallize was collected and a melting curve taken, m. p. $-13.2$ to $-12.2°$. The chloride was made from this alcohol in the same manner,[3] dried with calcium chloride and distilled, b. p. 86.0 to 86.1°.

**The Apparatus.**—The apparatus consisted essentially of a liter Pyrex flask surrounded by a suitable manually controlled furnace. The reaction flask was connected directly to a quartz spiral manometer used as a null point instrument, and connected to the evacuating system and the bulb containing the sample by an all glass valve of the Bodenstein design but seated with fused silver chloride as suggested by Bates.[4] The temperature of the reaction flask was measured by a thermocouple inserted in a well reaching to the center of the reaction flask.

The flask was first evacuated with a mercury vapor pump in series with an oil pump to a pressure of between $10^{-3}$ and $10^{-4}$ mm. About 200 mm. of the chloride to be used was then admitted into the flask, and the system again evacuated. In this way practically all of the air was rinsed out of the flask. It was found, however, that with no further treatment of the flask consistent results could not be obtained and the reaction proceeded quite rapidly; evidently this was caused by a heterogeneous reaction occurring on the walls of the flask. It was, therefore, found necessary to treat the flask and the best method evolved was to allow some of the chloride to decompose in the flask at about 500° and thus deposit a fine coherent coating of carbonized material over the surface of the glass. One or two such treatments for an unpacked flask were found to be sufficient to give consistent results which were not lowered upon further treatment. It was found that a long or a very thorough evacuation of the flask destroyed the usefulness of this carbon deposit, and that also if any oxygen were permitted to enter the flask after it had been so treated the heterogeneous reaction set in again and could not be removed except by burning off the carbon coating and retreating the flask. In order to prevent the destructive effects of allowing the flask to stand evacuated for any length of time, and also to decrease the likelihood of air leaking into the flask, each run was left in the flask until the next run was to be begun and then it was evacuated with the oil pump only.

The pressure on the outside of the quartz spiral manometer was adjusted to the initial pressure desired and the flask then filled. The reaction was followed by increasing the pressure on the outer side of the quartz spiral by definite and known amounts and taking the time at which the pointers crossed. By using this method it was possible to take readings as rapidly as every fourteen seconds. The results were plotted as log of the pressure of the chloride against the time, and the slope of the straight line drawn through these points was taken as the rate constant.

Both reactions apparently did not proceed to completion; this may be attributed to the presence of some inert material, or a partial decomposition having already occurred at the starting time, or to a chemical equilibrium. The reaction, however, was in all cases more than 90% complete, and correction was made for this in calculating the rate constants.

## Results and Interpretations.

—A summary of the rate constants and the experimental data for both of the chlorides may be found in Tables I and II. In Fig. 1 is shown a plot of a typical run. The decompositions were found to be homogeneous within the limit of experimental error. The runs whose numbers include the letter "p" were carried out in a packed flask having ten times the surface–volume ratio of the regular reaction flask. An example of the effectiveness of treating the flask to diminish the wall reaction

TABLE I

DECOMPOSITION OF *t*-BUTYL CHLORIDE

| Run | $T$, °K. | $P_0$ | $k \times 10^3$ sec.$^{-1}$ |
|---|---|---|---|
| 43 | 547.4 | 106.8 | 0.087 |
| 44 | 566.4 | 106.7 | .25 |
| 46 | 566.8 | 27.5 | .33 |
| 40 | 568.8 | 106.3 | .28 |
| 45 | 569.4 | 53.9 | .40 |
| 31 | 580.9 | 27.0 | .85 |
| 30 | 582.4 | 53.4 | .87 |
| 32 | 584.5 | 212.9 | .96 |
| 22p | 585.1 | 106.5 | 1.13 |
| 28 | 585.4 | 119.7 | 1.16 |
| 29 | 585.4 | 105.9 | 1.11 |
| 9 | 585.6 | 101.7 | 1.17 |
| 24p | 586.3 | 106.5 | 1.25 |
| 23p | 586.5 | 106.7 | 1.22 |
| 33 | 586.7 | 106.3 | 1.07 |
| 10 | 586.8 | 105.0 | 1.29 |
| 21p | 587.6 | 106.8 | 1.39 |
| 27 | 587.7 | 106.0 | 1.23 |
| 12 | 587.8 | 57.9 | 1.19 |
| 11 | 588.0 | 214.2 | 1.19 |
| 38 | 613.2 | 212.7 | 6.7 |
| 37 | 614.9 | 106.0 | 6.7 |
| 36 | 615.0 | 107.8 | 7.0 |
| 39 | 615.9 | 53.9 | 6.9 |
| 35 | 624.8 | 105.7 | 12.5 |

---

[3] "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1926, Vol. VI, p. 138.

[4] Cook and Bates, This Journal, 57, 1775 (1935).

TABLE II

DECOMPOSITION OF *t*-AMYL CHLORIDE

| Run | $T$, °K. | $P_0$ | $k \times 10^3$, sec.$^{-1}$ |
|---|---|---|---|
| 17 | 543.8 | 150 | 0.120 |
| 25p | 544.1 | 80 | .172 |
| 16 | 544.9 | 70 | .134 |
| 26p | 545.2 | 100 | .190 |
| 15 | 548.2 | 34 | .162 |
| 24p | 549.9 | 75 | .34 |
| 19 | 558.2 | 150 | .37 |
| 18 | 558.4 | 70 | .36 |
| 23 | 566.9 | 135 | .73 |
| 11 | 567.3 | 140 | .62 |
| 22 | 567.7 | 60 | .82 |
| 10 | 574.5 | 150 | 1.04 |
| 20 | 585.6 | 120 | 2.5 |
| 21 | 586.3 | 60 | 2.7 |
| 13 | 597.5 | 140 | 5.7 |
| 12 | 599.5 | 70 | 6.4 |
| 14 | 599.7 | 30 | 6.6 |

may be observed in the case of the *t*-amyl chloride. After three treatments—each consisting in allowing 200 mm. of the chloride to stand in the flask for eight hours at 500°—the rate of the reaction in the packed flask was 80% greater than the rates observed for the unpacked flask. After three more similar treatments, the rate was only 50% greater than for the unpacked flask, and after one more such treatment the rate was only 33% greater. This indicates a constantly decreasing rate approaching the minimum found for the unpacked flask. All runs using the packed flask were carried out at the lower temperatures since with these slow rates the catalyzed reaction became more noticeable.

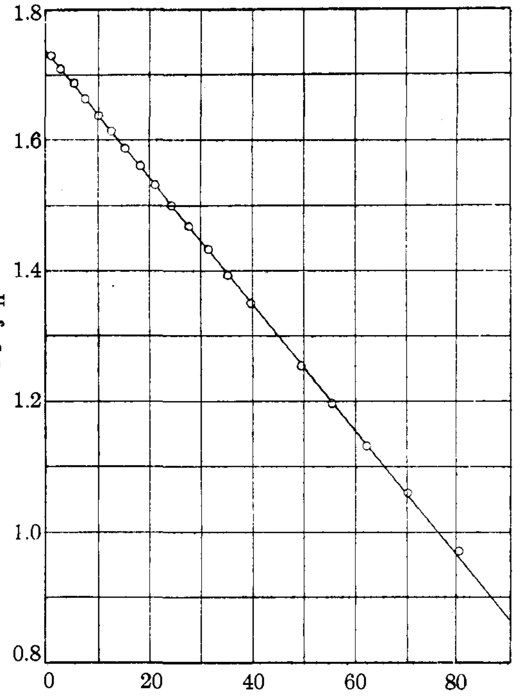


Fig. 1.—Plot of time against the logarithm of the pressure of the tertiary chloride for a typical run.

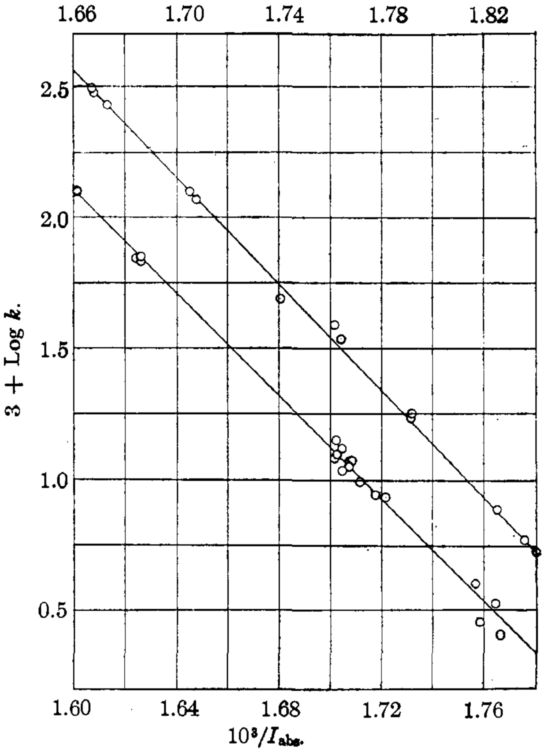


Fig. 2.—Plot of the reciprocal of the absolute temperature against the logarithm of the unimolecular rate constant. Lower curve refers to tertiary butyl chloride, and the upper curve to the tertiary amyl chloride.

The usual plot of log $k$ against the reciprocal of the absolute temperature, as illustrated in Fig. 2, resulted in straight lines for both chlorides, the slopes of which yielded the following energies of activation: for the *t*-butyl 45,000 ± 1900 calories, and for the *t*-amyl chloride an energy of 46,200 ± 700 calories. These may be considered to be identical within the limit of experimental error. Taking the weighted average of these—each being weighted by the reciprocal of the probable error—we find an average energy of activation of 46,000 calories. With this value of the activation energy the equation $k = Ae^{-E/RT}$ gives $A$ as $1.9 \times 10^{14}$ for the tertiary butyl chloride, and $4.5 \times 10^{14}$ sec.$^{-1}$ for the tertiary amyl chloride. Schultz and Kistiakowsky have interpreted their results as indicating a decrease of activation energy in changing from *t*-butyl to *t*-amyl alcohol. Such a trend is opposite to that found now with the chlorides and it appears likely that both are due to experimental errors. We have calculated, therefore, the probable limit of error of the activation energies of the *t*-butyl and *t*-amyl alcohols from the data of Schultz and Kistiakowsky[2] and found them to be 65,500 ± 7000 and 60,000 ± 3700 calories, respectively. These again are identical within the limit of experimental error. It is, therefore, quite legitimate to determine—in the same manner as has been done above for the chlorides—the weighted mean energy of activation for the two alcohols and attribute temporarily this energy to each. We find this mean energy to be 62,000 calories. Using this mean energy in the unimolecular equation the $A$ factor is $6.15 \times 10^{13}$ for the *t*-butyl alcohol, and $1.43 \times 10^{14}$ for the *t*-amyl alcohol, all quantities being expressed in inverse seconds.

In each case, thus, we notice an increase of 2.35-fold in the value of $A$ in going from the *t*-butyl to the *t*-amyl homolog; such an exact agreement may be a coincidence, of course. Quite recently Rice and Gershinowitz[5] have discussed the decomposition of the tertiary alcohols, arriving at some very interesting results. While their general method of approach seems to us to be very promising, we cannot quite agree with their interpretation of the reaction of the *t*-amyl alcohol which involves a removal of hydrogen atoms from the methyl group at the end of the $C_2H_5$. The result of such a process should be a ring formation or a temporary formation of a doubly unsaturated free radical or, finally, it must be accompanied by a *simultaneous* shift of another hydrogen atom. The first possibility is eliminated because there is no evidence whatever for a formation of ring compounds but these are not sufficiently unstable to decompose instantaneously,[6] particularly at the low temperatures involved in the decomposition of the chlorides. The second possibility would require much too high an activation energy and may be disregarded altogether. Against the third possibility we can offer no conclusive evidence. It seems to us, however, that it would not be directly comparable, either in the activation energy or in the $A$ factor, to a simple elimination of a hydrogen atom with a simultaneous formation of a double bond and in the following we shall proceed as if this possibility were eliminated also. The difference in the rates of the *t*-butyl and *t*-amyl compounds is to be attributed then to a different reactivity of the primary and the secondary hydrogens. Indeed, the organic evidence shows that in the case of *t*-amyl alcohol and chloride, the resulting hydrocarbon is predominantly trimethylethylene, meaning that the secondary hydrogens in the $C_2H_5$ group are more reactive than the primary ones in the two $CH_3$ groups. Applying now the method of Rice and Gershinowitz[5] we find that, per hydrogen, in the *t*-butyl compound, the $A$ factor is $6.85 \times 10^{12}$ and $2.11 \times 10^{13}$ for the alcohol and the chloride, respectively. The $A$ factors of the amyl compounds are then to be regarded as six times this quantity plus twice the $A$ factor of the secondary hydrogens. This gives for the latter quantities $5.01 \times 10^{13}$ and $1.61 \times 10^{14}$, respectively. Reasoning further along the general lines indicated by Eyring[7] and by Rice and Gershinowitz[5] it seems to us rather improbable that the $A$ factors of the primary and the secondary hydrogens should differ so much. Instead it is more reasonable to assign the apparent difference of the $A$ factors to a real (but concealed because of experimental uncertainties) difference of the activation energies of the two processes. Assigning now the same $A$ factor to the secondary hydrogens as was found, per hydrogen atom, for the butyl compounds, one finds the activation energies at the mean temperature of the experiments to be 3200 and 2400 calories less than those for the primary hydrogens, in the alcohols and the chlorides, respectively. The over-all observed activation energies of the *t*-amyl compounds should differ, therefore, by nearly this much from the butyl compounds.

These figures appear to agree exceptionally well with Eyring's[8] prediction of the differences in the binding energy of the two types of hydrogens, but not too much stress should be placed upon this agreement, by reason of the uncertainties in our own conclusions from the experimental results. However, the results of Ogg[9] on iodides are also probably better interpreted with identical $A$ factors but changing activation energies from which a similar decrease of the stability of the C–I bond in the series $CH_3I$, $C_2H_5I$, $C_3H_7I$ follows.

In any case the close agreement in the kinetics of the decomposition of the alcohols and the chlo-

---

[5] Rice and Gershinowitz, *J. Chem. Phys*., **3**, 490 (1935).

[6] Chambers and Kistiakowsky, THIS JOURNAL, **56**, 399 (1934).

[7] Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[8] Eyring, THIS JOURNAL, **54**, 3191 (1932).

[9] Ogg, *ibid.*, **56**, 526 (1934).

rides seems to eliminate altogether the possibility that these reactions are of a chain character. The activation energies are of course quite different, but this is in complete qualitative agreement with the greater strength of the C–OH than the C–Cl bond; the essential thing is that the *A* factors agree perfectly. It will indeed require a very vivid imagination to construct chain mechanisms which will give identical kinetics and nearly identical chain length in these reactions occurring at temperatures different by about 200°.

## Summary

The thermal decompositions of tertiary butyl and tertiary amyl chlorides have been investigated in the temperature region of 543–645°K.

The reactions are homogeneous, unimolecular, and have activation energies of 45,000 ± 1900 and 46,200 ± 700 calories, respectively, which are identical within experimental error.

The rate expressions are: $k = 1.9 \times 10^{14} e^{-46,000/RT}$ sec.$^{-1}$ for tertiary butyl chloride, and $k = 4.5 \times 10^{14} e^{-46,000/RT}$ sec.$^{-1}$ for tertiary amyl chloride if the activation energies are regarded as identical.

The data are compared to those recorded for *t*-butyl and *t*-amyl alcohols, and a possible meaning of the variation in the values of the *A* factor in the rate equation is discussed, the conclusion being reached that the activation energies of *t*-amyl compounds are slightly less than those of the *t*-butyl compounds.

MALLINCKRODT LABORATORY
CAMBRIDGE, MASS. RECEIVED NOVEMBER 8, 1935

---

[CONTRIBUTION FROM THE CHEMO-MEDICAL RESEARCH INSTITUTE, GEORGETOWN UNIVERSITY]

# The Colored Compound Formed in the Sullivan Reaction for Guanidine

BY M. X. SULLIVAN AND W. C. HESS

In a study of the relation of guanidine to health and disease, with particular reference to muscular dystrophies, Sullivan[1] devised a highly specific colorimetric test for guanidine, $NH{=}C(NH_2)_2$, not given by methyl guanidine or any other substituted guanidine, and sensitive to 0.1 mg. per cubic centimeter.

In order to determine the structure of the colored compound formed in the guanidine reaction, the complex was made on a larger scale, first in dilute solutions in the proportions used in the test and second in concentrated solutions of each reactant.

**Experiment I.**—To 165 mg. of guanidine hydrochloride (approximately 100 mg. of guanidine) in 100 cc. of water was added 100 cc. of 1% 1,2-naphthoquinone-4-sodium sulfonate. After the careful addition of 40 cc. of *N* sodium hydroxide, slowly with stirring, the mixture was brought to 90° and held there for one minute. On cooling and adding 50 cc. of concentrated hydrochloric acid and 50 cc. of concentrated nitric acid, a precipitate formed. This was centrifuged and washed five times with 10-cc. portions of water, with centrifuging after each addition, and with 20 cc. of acetone.

**Experiment II.**—To 165 mg. of guanidine hydrochloride in 10 cc. of water was added 1 gram of 1,2-naphthoquinone-4-sodium sulfonate suspended in 10 cc. of water and 1 cc. of 5 *N* sodium hydroxide, added dropwise with stirring. The mixture was brought to 90° and held there for one minute, cooled, acidified with 5 cc. of concentrated hydrochloric acid and 5 cc. of concentrated nitric acid and centrifuged. The precipitate was washed with 30 cc. of water in 10-cc. portions, with centrifuging after each addition, then with 10 cc. of equal parts of water and acetone followed by 20 cc. of acetone.

The materials dried to constant weight over calcium chloride in a desiccator, in both cases decomposed at about 250°. The nitrogen content was 19.33 and 19.19%, respectively.

Other samples were made with higher concentration of alkali and with the precipitant, hydrochloric acid alone, nitric acid alone, and mixtures of these acids. In all cases the decomposition point was the same and the nitrogen found was of the same order as given above. The average of six such preparations was 19.24% nitrogen for samples dried over calcium chloride in a desiccator. The average nitrogen for three preparations, one precipitated by concentrated hydrochloric acid, one by concentrated nitric acid, and one by hydrochloric acid and nitric acid was 19.10 for the desiccator dried sample and 19.59 for the same samples dried at 80–105°. Part of the apparent moisture on heating is due to slight decomposition.

Several possibilities as to the structure are possible. Thiele and Barlow[2] had prepared a beta naphthoquinone derivative of aminoguanidine by mixing a fresh solution of beta-naphthoquinone in alcohol with a mole of aminoguanidine in water in the presence of a few drops of nitric acid, boiling until an orange-yellow precipitate formed. To this complex they assigned the formula $C_{11}H_{10}N_4O$,

---

[1] Sullivan, *Proc. Soc. Exptl. Biol. Med.*, **33**, 106 (1935).

[2] Thiele and Barlow, *Ann.*, **302**, 311 (1898).