[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

# The Thermal and Hydrolytic Behavior of Imido and Thioimido Ester Salts[1]

BY RAYMOND H. HARTIGAN[2] AND JOHN B. CLOKE

Although considerable effort has been expended in a study of the action of heat[3] and water[4] on the ordinary imido ester salts, relatively little work has been conducted on the corresponding thioimido ester salts.[3c,5] The present paper constitutes an extension of the work on ordinary imido ester salts to the sulfur analogs in order to ascertain the comparative effects of oxygen and sulfur. A further purpose was to consider the relationship between the structures of thioimidobenzoate hydrochlorides, their stabilities to heat and water, and the basic strengths of the corresponding free thioimidobenzoates.

**Preparation of the Thioimidobenzoate Hydrochlorides.**—These derivatives were prepared in accordance with the method of Pinner[3c] by interaction of equivalent quantities of benzonitrile, mercaptan,[6] and dry hydrogen chloride in three or four times the volume of anhydrous ether. The solids which separated from the reaction mixtures were analyzed after storage *in vacuo* over solid sodium hydroxide and phosphorus pentoxide to remove any excess acid. Table I summarizes the yields and analytical data for the compounds investigated.

TABLE I

YIELDS AND ANALYSES OF THIOIMIDOBENZOATE HYDROCHLORIDES

| Compound | Yield, % | Analyses, % Calculated Cl | N | Found Cl[a] | | N[b] | |
|---|---|---|---|---|---|---|---|
| Methyl- | 75 | 18.89 | 7.46 | 18.96 | 18.85 | 7.45 | 7.40 |
| Ethyl-[c] | 90 | 17.58 | 6.94 | 17.43 | 17.80 | 6.85 | 6.88 |
| *n*-Propyl- | 61 | 16.44 | 6.49 | 16.42 | 16.62 | 6.61 | 6.53 |
| Isopropyl- | 53 | 16.44 | 6.49 | 16.50 | 16.41 | 6.57 | 6.55 |
| *n*-Butyl- | 78 | 15.43 | 6.10 | 15.40 | 15.48 | 5.98 | 5.93 |
| Isobutyl- | 74 | 15.43 | 6.10 | 15.36 | 15.20 | 5.99 | 6.03 |
| *t*-Butyl-[d] | 14 | 15.43 | 6.10 | 16.90 | 17.00 | 5.85 | 5.88 |
| *n*-Amyl- | 64 | 14.54 | 5.75 | 14.52 | 14.49 | 5.65 | 5.69 |
| Isoamyl-[e] | 43 | 14.54 | 5.75 | 14.49 | 14.42 | 5.67 | 5.65 |
| Phenyl-[f] | 40 | 14.20 | 5.61 | 14.23 | 14.00 | 5.56 | 5.50 |
| Benzyl-[c] | 51 | 13.44 | 5.31 | 13.45 | 13.39 | 5.43 | 5.30 |

[a] Computed from data obtained by extrapolation of reaction-rate curve back to zero time. [b] Micro-Kjeldahl method. [c] Prepared according to procedure of Bernthsen (ref. 5a). [d] The corresponding oxygen compound cannot be prepared by the method of Pinner. In the case of the thio-derivative, after passing hydrogen chloride into the reaction mixture and allowing the mixture to stand for five days, only a small amount of solid separated. Addition of a large quantity of petroleum ether did not improve the yield appreciably. This compound on standing over solid sodium hydroxide in a vacuum desiccator for two weeks still possessed a faint odor of hydrogen chloride. Insufficient material was available to make it worth while to recrystallize it from a halogenated hydrocarbon, such as chloroform, acetylene tetrachloride, β-trichloroethane, or pentachloroethane, in which these substances are soluble. It is interesting to note that the ethyl compound, which served as a basis for the solubility tests, failed to dissolve in tetrachloroethylene or in methylchloroform. [e] Prepared by method of Pinner, *Ber.*, **11**, 1825 (1878). [f] Prepared according to procedure of Autenrieth and Bruning (ref. 5b).

**Preparation of Ordinary Imido Ester Hydrochlorides.**—In order to obtain comparative data on the oxygen and sulfur derivatives, it was necessary to consider the thermal behavior of some of the imido ester salts synthesized by earlier workers in this Laboratory. These compounds were prepared by the general method of Pinner from nitrile, alcohol, and dry hydrogen halide. The particular procedure employed was determined by the general nature of the nitrile.

**Benz-imido Ester Salts.**—The method discussed for the corresponding thioimidobenzoate hydrochlorides proved satisfactory. In a few cases, where the removal of excess hydrohalogen acid was difficult or the salt was impure, solution of the substance in glacial acetic acid followed by precipitation with anhydrous ether gave a product of the desired purity.

**Aliphatic and Alicyclic Imido Ester Salts.**—The use of a diluent in the preparation of these compounds was detrimental and it was found important to employ only slightly more than the *theoretical* quantity of hydrogen halide. Although some of the salts set to a solid mass of crystals, most were of a viscous, oily character and required storage *in vacuo* over sodium hydroxide and phosphorus pentoxide, or even cooling to −70 to −80°, for complete solidification of the oil.[7]

## Part I

### Thermal Behavior of a Series of Thioimidobenzoate Hydrochlorides

The ordinary imido ester salt pyrolyzes irreversibly to give the corresponding amide and alkyl

---

(1) This paper is an abstract of the first part of a thesis presented by Raymond H. Hartigan to the Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Original manuscript received April 21, 1942.

(2) Present address, Mellon Institute of Industrial Research, Pittsburgh, Pa.

(3) (a) Pinner, *Ber.*, **16**, 355, 1654 (1883); (b) Beyer, *J. prakt. Chem.*, **28**, 190 (1883); (c) Pinner, "Die Imidoäther und ihre Derivate," R. Oppenheim, Berlin, 1892; (d) Lengfeld and Stieglitz, *Am. Chem. J.*, **16**, 70 (1894); Stieglitz, *ibid.*, **21**, 101 (1899).

(4) (a) Stieglitz with Derby, McCracken, and Schlesinger, *Am. Chem. J.*, **39**, 29, 166, 402, 437, 586, 719 (1908); Stieglitz, THIS JOURNAL, **32**, 221 (1910); *ibid.*, **34**, 1687 (1912); *ibid.*, **35**, 1774 (1913); (b) Carr, doctoral dissertation, University of Chicago, 1910; (c) Cloke, Knowles and Anderson, THIS JOURNAL, **58**, 2547 (1936); (d) Cloke and Keniston, *ibid.*, **60**, 129 (1938).

(5) (a) Bernthsen, *Ann.*, **197**, 348 (1879); (b) Autenrieth and Bruning, *Ber.*, **36**, 3465 (1903); (c) Schmidt, *ibid.*, **47**, 2545 (1914); (d) Steinkopf and Muller, *ibid.*, **56**, 1930 (1923); (e) Kaufmann and Adams, THIS JOURNAL, **45**, 1744 (1923).

(6) The mercaptans used were purified Eastman Kodak Company products, with the exception of methyl mercaptan which was prepared according to the directions of Kiprianov, Suitnikov and Suich, *J. Gen. Chem.* (U. S. S. R.), **6**, 576 (1936).

(7) The derivative from secondary butyl cyanide and ethyl alcohol failed to crystallize when subjected to this procedure.

halide. In the case of the thioimido ester salts, Bernthsen[5a] observed thioamide formation with ethyl imidobenzoate hydroiodide, and Pinner[8] showed that the ethyl thioimido-iso- and -terephthalate hydrochlorides behave similarly.

The thermal behavior of the thioimidobenzoate hydrochlorides discussed in this paper was followed by a differential thermocouple method.[9] From the data, the temperature range of the pyrolysis and a so-called "mean temperature of pyrolysis" were obtained.

In the work, one leg of a chromel–constantan thermocouple was immersed in approximately 0.5 g. of the sample[10] and the other in an equal amount of petrolatum. The two tubes were then heated uniformly[11] in a bath, and simultaneous readings were taken each minute on a thermometer and potentiometer. Figure 1 represents the results of a typical experiment on ethyl thioimidobenzoate hydrochloride. The curve shows two minima. The temperature corresponding to A has been taken as the "mean temperature of pyrolysis" of the compound. Point B, which always lies between 200 and 215°, is attributed to the further pyrolysis of the thiobenzamide formed from the thioimidobenzoate hydrochloride.[12] The characteristic "mean temperatures of pyrolysis" are given in Table II.

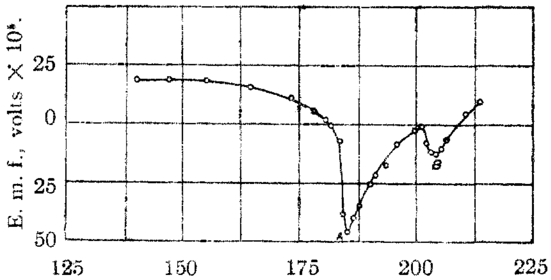


Fig. 1.—Pyrolysis curve for ethyl thioimidobenzoate hydrochloride.

TABLE II

THERMAL BEHAVIOR OF THIOIMIDOBENZOATE HYDROCHLORIDES[a]

| Compound | "Mean temperature of pyrolysis," °C. |
|---|---|
| Methyl- | 194 |
| Ethyl-[b] | 185 |
| *n*-Propyl- | 165 |
| Isopropyl- | 171 |
| *n*-Butyl- | 163 |
| Isobutyl- | 163 |
| *t*-Butyl- | 111 |
| *n*-Amyl- | 159 |
| Isoamyl- | 158 |
| Phenyl-[c] | 170 |
| Benzyl-[d] | 176 |

[a] In all cases except that of the phenyl compound the presence of thiobenzamide was proved by recrystallization of the residue and a melting point determination when heating was discontinued below the second break of the curve, or by the presence of the characteristic break above 200°. In most cases, also, there was at least a faint odor of mercaptan during the heating process. [b] Odor of ethyl chloride during the decomposition. [c] This compound pyrolyzes to give, chiefly, thiophenol, benzonitrile, and hydrogen chloride (ref. 5b). A small amount of solid substance of m. p. 231–233° appeared in the residue. [d] Sharp odor of benzyl chloride developed during the pyrolysis. [e] Individual determinations were usually within 3°.

We are led to conclude from the tabulated results that thioimido ester salts undergo two concurrent reactions when subjected to heat. In the first place, they pyrolyze normally according to the Pinner reaction to give the appropriate alkyl halide and thioamide, the latter decomposing further at the high temperatures into nitrile (or polymer) and hydrogen sulfide; and, in the second, they give nitrile, mercaptan, and hydrogen chloride. The alkyl thioimido ester salts are predominantly pyrolyzed in the normal way, the second reaction taking place to a minor extent. With the phenyl derivative, on the other hand, the latter reaction plays a major role.

It is interesting to note that the "mean temperatures of pyrolysis" of the sulfur derivatives containing normal radicals have the order: methyl > ethyl > propyl > butyl > amyl; also, for the iso-type radicals the order is, isobutyl > isoamyl. A plot of the "mean temperatures of pyrolysis" against the structures of the *n*-alkyl

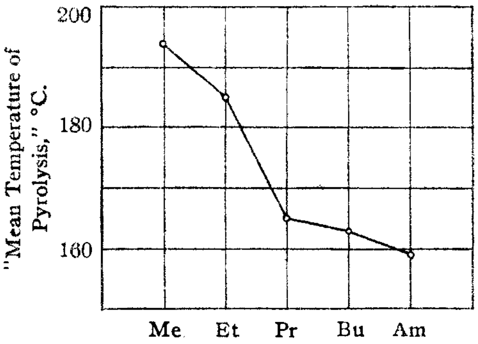


Fig. 2.—Relation between "Mean Temperatures of Pyrolysis" and structures of *n*-alkyl thioimidobenzoate hydrochlorides.

---

(8) Pinner, *Ber.*, **17**, 1428 (1884). Small amounts of hydrogen sulfide, mercaptan, and nitrile were produced in addition, however.

(9) Cloke, THIS JOURNAL, **51**, 1174 (1929). The heat effect measured represents the algebraic sum of the heat of decomposition of the material and the contribution due to the relative change with temperature of the physical properties of the reaction mixture and reference liquid under the controlled conditions of the experiment. The latter, doubtless, is of constant and relatively minor magnitude.

(10) Consistent values were obtained with samples weighing up to 1 g.

(11) While one would expect the results to be a function of the rate of heating, a rise in temperature of 0.5–2.0° per minute gave results for the "mean temperature of pyrolysis" agreeing within the limits of accuracy of the method.

(12) This was proved by the fact that a sample of thiobenzamide, heated under the conditions of the experiment to a temperature greater than 200°, gave a curve with a minimum at 214°. Benzonitrile and its polymers were also formed since the material remaining after the pyrolysis was semisolid, and possessed a strong odor of benzonitrile. This observation was previously reported by Henry, *Ann.*, **152** 148 (1869).

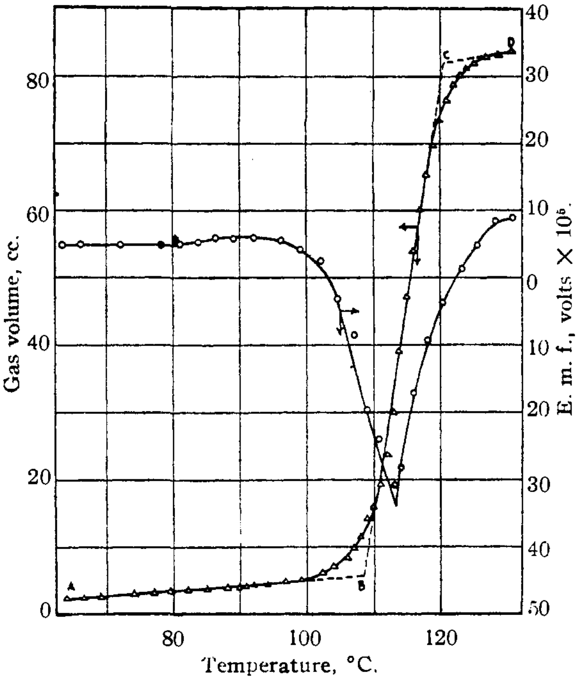


Fig. 3.—Pyrolysis curves for ethyl imidoacetate hydrochloride.

thioimidobenzoate hydrochlorides is shown in Fig. 2. This graph possesses an interesting alternation such as is common in homologous series. Melting points usually drop sharply from methyl to ethyl to propyl, and then change gradually. The "mean temperatures of pyrolysis" of the compounds studied vary similarly with structure.

It was thought worth while to follow by the same differential thermocouple method the action of heat on some of the ordinary imido ester hydrochlorides available in this Laboratory, and to compare the pyrolysis curves and "mean temperatures of pyrolysis" with those of the related sulfur compounds. Part II considers the thermal behavior of various types of imido ester salts.

## Part II

**The Thermal Behavior of Imido Ester Salts.**—The data for typical experiments by the differential thermocouple method on ethyl imidoacetate hydrochloride and ethyl imidoisobutyrate hydrochloride are plotted in Figs. 3 and 4, respectively. The former pyrolyzes without melting; the latter possesses a true melting point, and subsequently pyrolyzes. All the ordinary imido ester salts studied give one or the other of these two types of curves. None of the thioimidobenzoate hydrochlorides investigated shows a true melting point prior to pyrolysis under the controlled conditions of the experiment.

In order to be certain that the so-called "mean temperature of pyrolysis," which is the value at which the difference in temperature between the reaction mixture and the reference liquid is a maximum, characterizes the imido ester salts, the thermal behavior of those derivatives yielding gaseous alkyl halides was followed by a gas volumetric procedure.

For this work, a 75 × 16 mm. test-tube containing about 0.5 g. of sample was connected by means of thick-walled capillary tubing to a jacketed, gas-measuring buret through a three-way stopcock. Water of constant temperature was circulated through the jacket. The buret and side-tube were filled with mercury. The mixture was heated uniformly at the rate of 0.5–2.0° per minute in a bath and simultaneous readings of bath temperature and gas volume at atmospheric pressure were taken each minute. Norris and his associates[13] have drawn significant conclusions concerning the reactivity of atoms and groups in organic molecules from pyrolysis temperatures, measured by a procedure employing the same fundamental principle.

In Figs. 3 and 4 graphs of the volumes of alkyl halide against bath temperatures are superimposed on the e. m. f. curves for the corresponding imido ester salts. The steep portions, BC, of the curves represent the true ranges of pyrolysis.

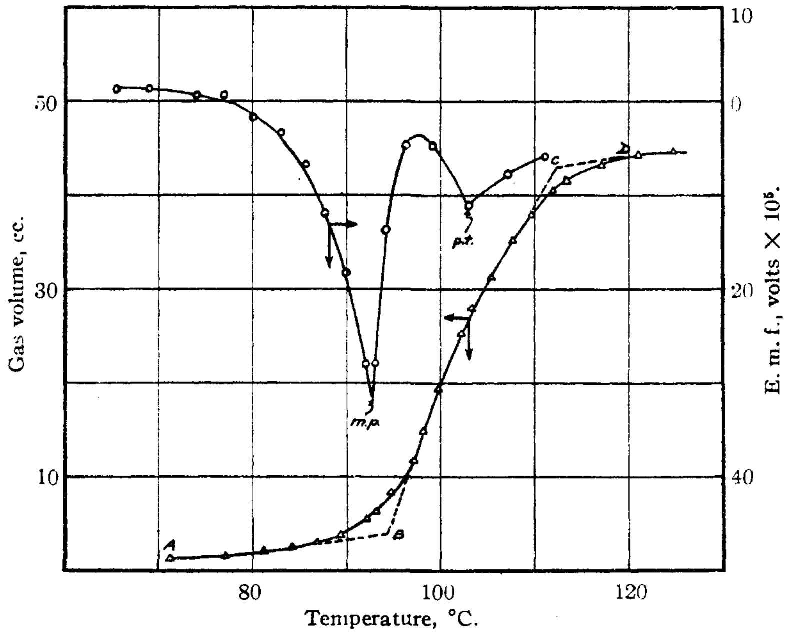


Fig. 4.—Pyrolysis curves for ethyl imidoisobutyrate hydrochloride.

---

(13) (a) Norris and Young, THIS JOURNAL, **52**, 753 (1930); (b) *ibid.*, **52**, 5066 (1930); (c) Norris and Thomson, *ibid.*, **53**, 3108 (1931); (d) Norris and Tucker, *ibid.*, **55**, 4697 (1933); (e) Norris and Cresswell, *ibid.*, **55**, 4946 (1933); (f) **56**, 423 (1934).

Comparison indicates that the differential thermocouple method adequately measures the region of pyrolysis, and the results for the "mean temperatures of pyrolysis" by this method have been shown to be consistent within 2 to 3°. Table III lists the "mean temperatures of pyrolysis" of a number of imido ester salts obtained by the differential thermocouple method.

TABLE III

"MEAN TEMPERATURES OF PYROLYSIS" OF IMIDO ESTER SALTS

| Ethyl imido ester hydrochlorides | "Mean temperature of pyrolysis," °C. |
|---|---|
| -Acetate[3a,14] | 113 |
| -Propionate[3a,14] | 99 |
| -Butyrate[4b] | 98 |
| -$\gamma$-Chlorobutyrate[18a] | 98 |
| -Isobutyrate[4b] | 103 |
| -Valerate[4b] | 97 |
| -Isovalerate[4b] | 97 |
| -Pivalate[15] | 110 |
| -Benzoate[3a,c,4a] | 118 |
| -Phenylacetate[16] | 102 |
| -Cyclopropanecarboxylate[4c] | 110 |
| -1-Phenylcyclopropanecarboxylate[4c] | 103 |
| -Cyclobutanecarboxylate[12b] | 92 |
| -1-Phenylcyclobutanecarboxylate[18b] | 115 |
| Imidobenzoate hydrochlorides | |
| Ethyl- | 118 |
| $\beta$-Bromoethyl-[18c] | 134 |
| $\beta$-Chloroethyl-[17] | 142 |
| $\alpha$-Methyl-$\beta$-chloroethyl-[18d] | 145 |
| $\gamma$-Bromopropyl-[18d] | 112 |
| $\gamma$-Chloropropyl-[4d] | 104 |
| $n$-Butyl-[18e] | 104 |
| $\delta$-Chlorobutyl-[18d] | 109 |
| Cyclopentyl-[18f] | 114 |
| Cyclohexyl-[18g] | 129 |
| Ethyl imidobenzoate hydrobromide[19] | 111 |

The imido ester salts studied are pyrolyzed normally to give the corresponding amide and alkyl halide. A comparison of the "mean temperatures of pyrolysis" of these oxygen derivatives with those of the sulfur compounds in Table II indicates that the thio compounds are considerably more stable. In general, the ordinary imido ester salts show little difference in their "mean temperatures of pyrolysis."

## Part III

## The Hydrolytic Behavior of a Series of Thioimidobenzoate Hydrochlorides

**Rates of Reaction.**—In aqueous solution ordinary imido ester salts undergo two simultaneous reactions. The first, which is accelerated by bases, is their decomposition into nitrile, alcohol (or phenol), and hydrogen chloride, whereas the second, favored by acids, is the formation of the corresponding ester plus ammonia. The usual alkyl imido ester hydrochlorides, therefore, are normally hydrolyzed to give the ordinary ester and ammonium chloride

$$RC({=}NH_2{}^+Cl^-)OR' + H_2O \longrightarrow RCOOR' + NH_4{}^+Cl^-$$

in accordance with the monomolecular law, although some of them undergo significant decomposition into the starting materials from which they are prepared. An extensive study of the action of water on ordinary imido ester salts has been made by Stieglitz and his collaborators[4a,b] and, more recently, by Cloke and his associates.[4c,d] The measurements reported in this section were made in order to compare the characteristics of the thioimido ester salts with those of their oxygen analogs.

The rates at which the thioimidobenzoate hydrochlorides react in the normal way were ascertained by the method of Stieglitz and Derby[20] for the analogous oxygen compounds. This method is based on the facts that the free thioimido ester can be liberated from its salt by the action of sodium hydroxide, and the free base, unlike ammonia, may be extracted from its aqueous solution by carbon tetrachloride.

In the work recorded in the following table, a 0.05 molar aqueous solution of the thioimido ester salt was prepared and maintained at a known temperature in a thermostat. Without delay, a 10-ml. volume of the reacting solution was pipetted into a Squibb funnel which contained a carefully measured volume of 0.1 $N$ sodium hydroxide and a suitable quantity of purified carbon tetrachloride. The mixture was at once well

TABLE IV

RATE OF REACTION OF $n$-PROPYL THIOIMIDOBENZOATE HYDROCHLORIDE WITH WATER AT 25°

Reaction: $C_6H_5C({=}NH_2{}^+Cl^-)SC_3H_7 + H_2O \rightarrow C_6H_5COSC_3H_7 + NH_4{}^+Cl^-$; $t$ = time in minutes from moment of dissolving; $a$ = molar concentration of original solution = 0.0484; $(a - x)$ = molar concentration of thioimido ester salt at time, $t$; $V_b$ = volume of base in ml.; $V_a$ = volume of 0.0975 $N$ acid; 10 ml. of base = 10.73 ml. of acid.

| $t$ | $V_b$ | $V_a$ | $(a - x)$ |
|---|---|---|---|
| 0 | .. | .. | .... |
| 7 | 10 | 5.80 | 0.0481 |
| 240 | 10 | 6.45 | .0417 |
| 540 | 10 | 7.23 | .0341 |
| 1380 | 10 | 8.75 | .0193 |
| 2670 | 10 | 9.50 | .0120 |

---

(14) Reitter and Hess, *Ber.*, **40**, 3022 (1907).

(15) Freund and Lenze, *ibid.*, **24**, 2155 (1891).

(16) Luckenbach, *ibid.*, **17**, 1421 (1884).

(17) Gabriel and Newmann, *ibid.*, **25**, 2384 (1892).

(18) Compounds originally reported in unpublished "Theses," Rensselaer Polytechnic Institute, by (a) P. L. Thompson (1930); (b) H. D. Kluge (1941); (c) W. R. Adams (1929); (d) D. T. Rogers (1931); (e) L. F. Heslin (1926); (f) E. D. Tierney (1929); (g) E. T. Candee (1927).

(19) The reported "mean temperature of pyrolysis" was measured on a recrystallized sample. The crude salt, containing excess hydrobromic acid, possessed a "mean temperature of pyrolysis" of 109°. Impurities of this type do not, therefore, appreciably affect the "mean temperature of pyrolysis."

(20) See ref. 4a, especially pp. 439-441.

shaken, the carbon tetrachloride layer drawn off, and the extraction repeated twice with fresh portions of this solvent. Finally, the residual alkaline solution was titrated with 0.1 $N$ mineral acid. Table IV gives the data for an experiment on the $n$-propyl compound.

The data for the various experiments were plotted (see Fig. 5, curve A) and the velocity constants, $k_s$, computed graphically using the equation for a monomolecular reaction.

Table V presents a summary of the velocity constants, $k_s$, obtained for the compounds investigated and, also, the values, $k_o$, for the corresponding oxygen derivatives, taken from the work of Stieglitz, Cloke and their associates.

TABLE V

VELOCITY CONSTANTS FOR THE HYDROLYSIS OF ORDINARY IMIDO- AND THIOIMIDOBENZOATE HYDROCHLORIDES AT 25°

| Compound | $k_o$, min.$^{-1}$ | $k_s$, min.$^{-1e}$ | $k_o/k_s$$^{e}$ |
|---|---|---|---|
| Methyl- | 0.00562[b] | 0.000914 | 6.1 |
| Ethyl- | .00307[b] | .000751 | 4.1 |
| *n*-Propyl- | .00295[b] | .000664 | 4.4 |
| Isopropyl- | .00103[b] | .000652 | 1.6 |
| *n*-Butyl- | .00291[c] | .000716 | 4.1 |
| Isobutyl- | .00300[d] | .000711 | 4.2 |
| *t*-Butyl- | ...... | .00135 | ... |
| *n*-Amyl- | ...... | .000693 | ... |
| Isoamyl- | .00291[d] | .000940 | 3.1 |
| Phenyl-[a] | ...... | ...... | ... |
| Benzyl- | ...... | .00184 | ... |

[a] The compound decomposed immediately, and almost completely, into thiophenol, benzonitrile and hydrogen chloride. Slight amounts of ammonia and thiol ester were also formed. The oxygen compound behaves similarly. [b] Taken from data of Derby (ref. 4a). [c] Taken from data of Heslin (ref. 18e). [d] Taken from data of McCracken (ref. 4a). [e] The figures given are average values, the variation of individual determinations being less than 1% from the mean.

The velocity constants of the methyl and ethyl derivatives were also determined at 0°. From the values at the two temperatures an energy of activation of 20,000 cal. was computed for both compounds. The data of Derby on the corresponding imidobenzoate hydrochlorides yield a result agreeing within the experimental error. Therefore, the differences in the rates of hydrolysis are to be attributed to the frequency factor in the rate equation.

It is evident from the study of the rates of reaction that thioimido ester salts undergo the same type of reaction with water as do their oxygen analogs,[21] although the former are considerably less sensitive to decomposition. The high instabilities of the $t$-butyl and benzyl compounds, relative to the other members of the series, are worthy of mention. If we arrange the thioimidobenzoate salts according to their stabilities toward water, the following order exists: isopropyl > $n$-propyl > $n$-amyl > isobutyl, $n$-butyl > ethyl > methyl > isoamyl > $t$-butyl > benzyl. In Table V one observes also that the ratio, $k_o/k_s$, averages 4.2 for the primary alkyl radicals. The value, 6.1, for methyl is higher than for the rest, as it is in the rate and limit of esterification of an acid. A value, 1.6, is found for the secondary group, isopropyl. Reid and his co-workers have shown mercaptans to occupy the same relative positions as alcohols in esterification, but the limit is far lower with mercaptans.

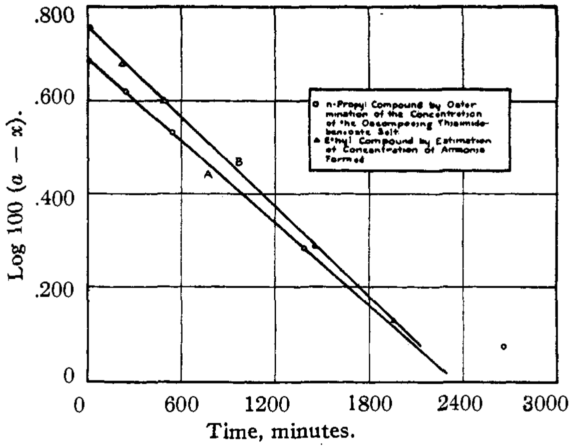


Fig. 5.—Hydrolysis curves for thioimidobenzoate hydrochlorides.[22]

Figure 6 expresses the relation between the velocity constants, $k_o$ and $k_s$, for hydrolysis and the structures of the normal alkyl imido- and thioimidobenzoate hydrochlorides, respectively. These curves are similar in shape, and their shapes resemble the graph of the "mean temperatures of pyrolysis" plotted against the structures of the sulfur compounds. This similarity is brought out clearly in Fig. 7, where there appears to be a linear relationship between the logarithms of the velocity constants for hydrolysis and the corresponding "mean temperatures of pyrolysis" of the $n$-alkyl thioimidobenzoate hydrochlorides. In these figures, also, one observes the anomalous behavior of the methyl derivative.

---

(21) The abnormal decomposition into the original materials, nitrile, mercaptan, and hydrogen chloride, is probably more significant, however, than in the case of the oxygen derivatives (see, *e. g.*, ref. 5d).

(22) With all the thioimidobenzoate hydrochlorides studied it was observed that when the compound had been somewhat more than half decomposed the points began to lie above the line (see curve A), and this became more pronounced as the reaction proceeded. The strong odor of mercaptan throughout the reaction suggested that the concurrent decomposition of the salt into mercaptan, nitrile, and hydrogen chloride, and/or the secondary hydrolysis of the thiol ester, formed by the normal reaction, were interfering (in the latter connection, see the work of Reid and his collaborators, *Am. Chem. J.*, **43**, 489 (1910); THIS JOURNAL, **37**, 1934 (1915); **38**, 2746, 2757 (1916); **39**, 1930 (1917); **40**, 569 (1918)). In order to test the validity of the velocity constants, based on the earlier stages of the reaction, the normal reaction was followed quantitatively in the case of the ethyl compound by estimating the amount of ammonia produced at different times, using a micro-Kjeldahl apparatus. Curve B was obtained from these data. The average of seven determinations of $k_s$ by this method was 0.000751, which is identical with that obtained by the simpler Derby method for the ethyl derivative.

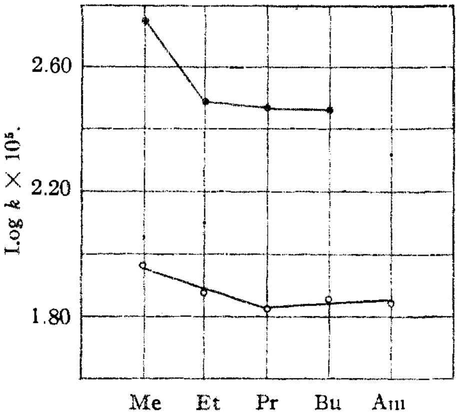


Fig. 6.—Relation between velocity constants, $k_o$ and $k_s$, for hydrolysis and structures of *n*-alkyl imido- and thioimidobenzoate hydrochlorides: ●, oxygen derivatives; ○, sulfur derivatives.

**Hydrolysis and Dissociation Constants.**—This work was conducted in order to compare the basic strengths of imido- and thioimido esters. The hydrogen ion concentration method was employed. For this purpose the Coleman glass electrode was found to be satisfactory.[23] However, in order to use this method it was necessary to take simultaneous readings of time and *p*H, and to extrapolate the practically linear values back to the time of preparation of the solution to ascertain the *p*H of the undecomposed thioimido ester salt solution.

In the experimental work, the appropriate quantity of the salt was dissolved at a noted time in water at 25°. The solution was then poured into the glass electrode vessel attached to the reference electrode, both sections being jacketed with water at 25°, and the *p*H measured at regular time intervals. Table VI gives the significant data for the methyl compound.

TABLE VI

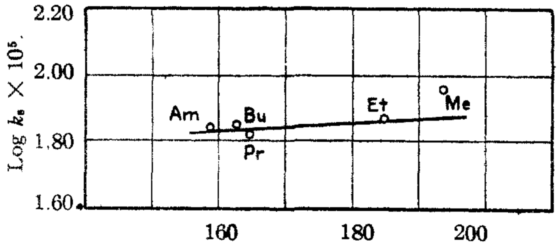
HYDROLYSIS CONSTANT OF METHYL THIOIMIDOBENZOATE HYDROCHLORIDE AT 25°

$C$ = molar concentration of salt solution; $\alpha$ = degree of hydrolysis; $K_h$ = hydrolysis constant.

| $C^a$ | *p*H | $H^+ \times 10^4$ | $\alpha \times 10^3$ | $K_h \times 10^7$ |
|---|---|---|---|---|
| 0.0313 | 3.64 | 2.29 | 7.32 | 16.9 |
| .0310 | 3.63 | 2.34 | 7.55 | 17.8 |
| .0154 | 3.82 | 1.51 | 9.80 | 14.9 |
| .0161 | 3.84 | 1.45 | 9.00 | 13.2 |
| .00825 | 3.92 | 1.20 | 14.6 | 17.8 |
| .00759 | 4.00 | 1.00 | 13.2 | 13.4 |
| .00478 | 4.17 | .676 | 14.2 | 9.8 |
| .00435 | 4.14 | .724 | 16.7 | 12.3 |

Av. $K_h = 14.5 \times 10^{-7}$

[a] Concentrations of $M/32$, $M/64$, $M/128$, $M/256$ were used by Stieglitz and his associates.



"Mean Temperature of Pyrolysis," °C.

Fig. 7.—Relation between velocity constants, $k_s$, for hydrolysis and "Mean Temperatures of Pyrolysis" of *n*-alkyl thioimidobenzoate hydrochlorides.

The dissociation constant of the base, $K_b$, may be computed from the equation, $K_b = K_w/K_h$, giving $K_b = (1.02 \times 10^{-14}/14.5 \times 10^{-7}) = 7.03 \times 10^{-9}$. Table VII presents a summary of the dissociation constants of the various members of the series and also of their oxygen analogs.

TABLE VII

DISSOCIATION CONSTANTS OF ORDINARY IMIDO- AND THIOIMIDOBENZOATES AT 25°

| Compound | $K_b^o \times 10^9$ | $K_b^s \times 10^9$ |
|---|---|---|
| Methyl- | 4.01[b] | 7.03 |
| Ethyl- | 9.08[b] | 11.2 |
| *n*-Propyl- | 13,1[b] | 7.86 |
| Isopropyl- | 15.3[b] | 9.18 |
| *n*-Butyl- | 12.4[c] | 6.21 |
| Isobutyl- | 10.6[d] | 5.98 |
| *t*-Butyl- | .... | 0.574 |
| *n*-Amyl- | .... | 3.19 |
| Isoamyl- | 14.3[d] | 3.68 |
| Phenyl-[a] | .... | 0.303 |
| Benzyl- | .... | 0.270 |

[a] The value obtained for the phenyl compound has little significance since this substance reacts abnormally with water. [b] Computed from data of Derby. [c] Computed from data of Heslin. [d] Computed from data of McCracken.

It may be seen that the ordinary and thioimido esters are comparable in their strengths as bases. In the oxygen series, Stieglitz observed that the order of the dissociation constants represents, inversely, the order of arrangement for the velocity constants for hydrolysis.[24] No such clear-cut relationship exists in the case of the sulfur analogs, although certain comparisons may be made. Thus, the benzyl and *t*-butyl compounds are salts of thioimido esters which are the weakest bases of this type, and at the same time, they react with water with the greatest rapidity, The isoamyl derivative is relatively unstable, and the base derived therefrom is among the weaker members. The values of the velocity constants

---

(23) The validity of the glass electrode method was proved by the fact that the determination of the hydrolysis constant of cyclohexyl imidobenzoate hydrochloride gave an average result of $3.56 \times 10^{-7}$. Candee (ref. 18g) obtained the value, $3.57 \times 10^{-7}$ by the Bredig conductivity method, used by Stieglitz and his associates, and $3.68 \times 10^{-7}$ by the quinhydrone electrode method of Cloke and Keniston (ref. 4d).

(24) The order of the dissociation constants is: isopropyl > isoamyl > *n*-propyl > *n*-butyl > isobutyl > ethyl > methyl, that of the values of $k_o$ being just the reverse (except for the *n*-butyl compound).

for the *n*-butyl and isobutyl compounds are of intermediate magnitude, as are their dissociation constants. Coming to the most stable derivatives, the *n*-propyl and isopropyl, the derived bases are stronger than any of the members of the series, with the exception of the ethyl compound. However, the methyl, ethyl, and *n*-amyl compounds show no such correlation.

**Acknowledgment.**—The authors wish to thank Mr. Robert E. Powers for aid in the preparation of the manuscript.

### Summary

1. Seven previously unreported thioimidobenzoate hydrochlorides in a series of eleven compounds have been prepared by the general method of Pinner.

2. The thermal behavior of the series has been investigated. It has been shown that they pyrolyze according to the Pinner reaction giving the corresponding thioamide and alkyl halide, although minor quantities of benzonitrile, mercaptan, and hydrogen chloride are also produced. They are considerably more stable than the analogous oxygen compounds.

3. Characteristic "mean temperatures of pyrolysis" are reported for this series and for a variety of ordinary imido ester salts.

4. Alkyl thioimidobenzoate salts react normally with water giving thiolesters and ammonium chloride, although the abnormal reaction yielding benzonitrile, mercaptan, and hydrogen chloride occurs to some extent. The hydrolytic stability of these substances is also greater than that of the corresponding oxygen derivatives.

5. The data suggest a linear relationship between the logarithms of the velocity constants for hydrolysis and the "mean temperatures of pyrolysis" of the *n*-alkyl thioimidobenzoate hydrochlorides.

6. The phenyl derivative behaves abnormally when subjected to the action of heat and water.

7. The dissociation constants of the thioimido esters have been determined, and in their strengths as bases these substances are found to be comparable with the ordinary imido esters. The general relationship of high velocity constant and low dissociation constant, reported previously for the oxygen compounds, does not exist for the sulfur derivatives, although some of the data are in harmony with this view.

TROY, NEW YORK RECEIVED FEBRUARY 12, 1945

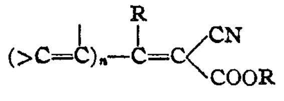
---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# Polyenes. III. The Absorption Spectra of Some Alkylidene Derivatives of Cyanoacetic Acid and its Esters[1]

BY LAWRENCE J. ANDREWS, STANLEY J. CRISTOL, SEYMOUR L. LINDENBAUM AND WILLIAM G. YOUNG

Recent experiments performed in this Laboratory have been directed toward the preparation of conjugated polyenes through the condensation of cyanoacetic acid and its esters or their alkylidene derivatives with unsaturated aldehydes and ketones. In searching for a simple method of detecting variations in the positions of the unsaturated linkages from those anticipated from the method of synthesis, a detailed study of the absorption spectra of compounds of the type



$$(>\mathrm{C}=\overset{|}{\mathrm{C}})_n-\overset{\overset{\mathrm{R}}{|}}{\mathrm{C}}=\mathrm{C}\begin{matrix}\diagup\mathrm{CN}\\ \diagdown\mathrm{COOR}\end{matrix}$$

R = H, $CH_3$ or $C_2H_5$

has been undertaken. The present investigation has been concerned with compounds in which *n* in the above formula equals 0, 1 or 2. This study has been pursued mainly to determine the effects on spectra of increasing the number of ethylenic linkages in conjugation with the cyano and carboxyl groups. Attention has also been given to the effects of introducing side chain methyl substituents onto the olefinic linkages, and a comparison of the spectra of the carboxylic acids with those of their esters has been made.

The compounds chosen to represent the case $n = 0$ in the above formula were methyl isopropylidenecyanoacetate, ethyl 1-methylpropylidenecyanoacetate, α-cyanocrotonic acid and its methyl ester, the preparations of which have all been described previously.[2] The compounds of the group $n = 1$, citrylidenecyanoacetic acid, α-cyanosorbic acid and α-cyano-δ-methylsorbic acid were prepared, respectively, by the condensation of citral, crotonaldehyde and β-methylcrotonaldehyde with cyanoacetic acid. The methyl esters of the two substituted sorbic acids were prepared by the silver salt–methyl iodide method. As representatives of the group $n = 2$, β-ionylidenecyanoacetic acid and its methyl ester[3] were used. The α isomers of these compounds[3] were considered in the $n = 1$ series.

The ultraviolet absorption spectra of these compounds in 95% ethanol solution were measured on the Beckman Spectrophotometer. The values of the maximum molecular extinction coefficient, ε, and the corresponding wave lengths of maximum absorption are listed in Table I. The absorption curves are given in Fig. 1.

---

[1] This work was made possible by a research grant from Sharp and Dohme, Inc.

[2] (a) Cope, THIS JOURNAL, 63, 3452 (1941); (b) Young, Andrews, Lindenbaum and Cristol, *ibid.*, 66, 810 (1944).

[3] Young, Andrews and Cristol, *ibid.*, 66, 520 (1944).