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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. XI. THE INFLUENCE OF THE STRUCTURE OF THE SUBSTITUENT ON THE TEMPERATURE OF DECOMPOSITION OF CERTAIN DERIVATIVES OF MALONIC ACID

BY JAMES F. NORRIS AND RALPH C. YOUNG

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For a number of years a major problem in this Laboratory has been the study of the influence of the structure of substituents on the lability of the atomic linkings in certain organic compounds. In the earlier work[1] the rates were determined at which such linkings were severed when analogous compounds reacted with a fixed reagent under the same conditions. An interpretation of these results led to conclusions in regard to the effect of the structure of a radical on the lability of certain bonds. In the last communication on this subject[2] a second method of comparing the relative lability of bonds was described. The temperatures at which the C—O bond was broken by heat alone in compounds of the type $(C_6H_5)_3C$-OR were determined. It was shown that these temperatures could be determined in separate experiments within $\pm 2°$ when the substances were heated under fixed conditions. A comparison of the averages of the values obtained in this way in the case of ten ethers with those obtained from the study of the same bond by means of reaction velocities brought out the striking fact that the two methods gave comparable results. There appears, therefore, to be a relation between the temperature at which a bond is broken by heat and the rate at which it is broken when a chemical reaction involving this bond takes place.

This conclusion appeared to be sufficiently important to warrant further investigation. Malonic acid and its derivatives of the type $RHC(COOH)_2$ decompose smoothly when heated into RH_2CCOOH and CO_2. Several such derivatives were made and the temperatures at which the decomposition began were determined. In the case of these compounds a C—C bond is broken. In the case of the esters previously studied a C—O bond was severed. It was of interest to discover if there was any relationship between the influence of the change in the alkyl radical, R, on the temperatures of pyrolysis in the two series.

In Table I are given the temperatures of decomposition of the derivatives of malonic acid and for comparison the temperatures of decompo-

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[1] (a) Norris and others, THIS JOURNAL, **47**, 837 (1925); (b) **49**, 2640 (1927); (c) **50**, 1795 (1928); (d) **50**, 1804 (1928); (e) **50**, 1808 (1928); (f) **50**, 1813 (1928); (g) **50**, 3042 (1928).

[2] Norris and Young, *ibid.*, **52**, 753 (1930).

Table I

Experimental Data

Radical	Temp. (°C.) of decomposition RHC(COOH)$_2$	Difference in decomp. temp.	Temp. (°C.) of decomposition RO—C(C$_6$H$_5$)$_3$	Difference in decomp. temp.	Vel. constants RO—H with p-NO$_2$C$_6$H$_4$COCl
None	128				
		8			
Methyl	120		262		0.184
		10		20	
Ethyl	110		242		.85
		11		12	
n-Propyl	99		230		.066
		9		9	
n-Butyl	108		239		.074
		18		19	
Isopropyl	90		220		.010

sition of the triphenylmethyl ethers containing the same alkyl radicals. There is also included the velocity constants of the reactions between *p*-nitrobenzoyl chloride and the alcohols containing these radicals.

It will be seen from the figures in the table that the temperatures at which decomposition takes place decrease as the radical is changed from methyl to ethyl and to *n*-propyl, but increase when *n*-propyl is replaced by *n*-butyl. This holds true in both series of compounds.

It is also a striking fact that the actual changes of the decomposition temperatures are the same in the two series, within the limits of accuracy of measurement, except in the case of the replacement of the methyl radical by ethyl.

In the two series the temperatures of decomposition fall in the same order as the velocity constants of the reactions between *p*-nitrobenzoyl chloride and the alcohols containing the same alkyl radicals present in the acids and ethers.

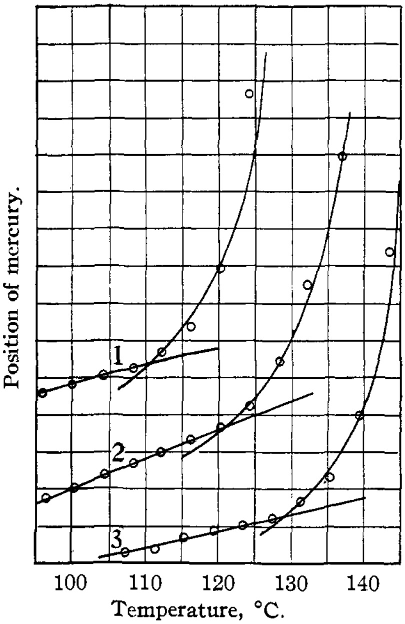
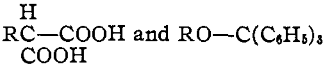


Fig. 1.—Position of mercury above an arbitrary zero for various values of the temperature. Each division = 10 cm. displacement: 1, ethylmalonic acid; 2, methylmalonic acid; 3, malonic acid.

The position of the changing substituent relative to the bond severed is the same in the two series of compounds. In both cases the substituent is in combination with an element

(C or O) a second bond of which is severed by heat. This is made clear by writing the formulas of the two classes of compounds as follows, and indicating the bonds which are severed in pyrolysis



$$\overset{H}{\underset{COOH}{RC}}\text{—COOH and RO—C}(C_6H_5)_3$$

The interpretation of the results leads to a reasonable conclusion. The change in the nature of R affects the strength of the linking between the radical and the carbon atom in one series and the oxygen atom in the other. These changes affect, in turn, the strength of the bond between these elements and the groups which are removed as the result of pyrolysis. The results furnish, thus, experimental evidence of the interrelationship between the affinities of an atom. It was an unexpected fact that the effects on the strength of the bonds of the carbon atom and of the oxygen atom were approximately the same with the same change in radical when measured by the change in temperature necessary to bring about the rupture of the bonds of the two elements.

Other cases of the effect of varying substituents on the temperature at which definite bonds are broken by heat are now being studied to discover if the simple relationships here emphasized are general. Work on certain aliphatic hydrocarbons is well advanced.

Experimental Details

Preparation of the Acids Used.—The derivatives of malonic acid were prepared in the usual way from ethyl malonate. The acids were crystallized from benzene several times until the behavior was constant when melting points were determined.

Method of Determining Decomposition Temperatures.—The method used was similar to that described in the paper on the pyrolysis of certain triphenylmethyl-alkyl ethers.[2] It consisted, in brief, in heating the material in a closed glass tube connected with a horizontal capillary tube containing a drop of mercury, and recording from time to time the position of the mercury on a scale as the temperature was raised at a definite rate. At the decomposition point there was a marked increase in the rate in the change of position of the mercury. One-half gram of malonic acid and equivalent amounts of the other acid were used in the experiments. The temperature of the bath was allowed to rise one degree in approximately forty-five seconds. The observations were plotted and curves drawn through the points recorded.

The accompanying plot indicates the nature of the curves obtained with three of the acids studied. The values of the decomposition temperatures recorded were obtained by plotting all the results accurately on a large scale.

The procedure described above was checked, in the case of malonic acid, by a chemical method. The acid was heated in a tube connected with another containing a solution of barium hydroxide. Air free from carbon dioxide was drawn rapidly through the two tubes, and the acid and the solution were then introduced. The stream of air was continued, and the tube containing the acid was heated at such a rate that the temperature rose about one degree per minute. The temperature observed when the first opalescence appeared in the barium hydroxide was taken as the decomposition temperature. The results obtained in this way in separate experiments agreed with those obtained by the physical method to within ±1°.

In Table II are given the melting points and decomposition temperatures of the acids as observed by the authors and the previously published values recorded in Beilstein's "Handbuch." The two sets of numbers in the column headed "Temperature of Decomposition Observed by Authors" are the results of independent experiments.

Table II

Melting Points and Decomposition Temperatures of Derivatives of Malonic Acid

Acid	Melting points (°C.) observed by authors	Melting points (°C.) recorded in Beilstein	Decomp. temp. (°C.) observed by authors		Decomp. temp. (°C.) recorded in Beilstein
Malonic	129–131	130.5 to 135.6	127	129	140–150
Methylmalonic	120–122	125 to 135	120	120	120
Ethylmalonic	110–111.5	111.5	110	110	160
n-Propylmalonic	94–96	96.0	100	98	150
n-Butylmalonic	99.5–101.5	101.5	108	108	150
Isopropylmalonic	85–87	87.0	90	90	120

The melting points were determined in the usual way in capillary tubes. The lack of sharpness in these values was no doubt due to the fact that they lie so close to the temperatures at which decomposition takes place.

The decomposition temperatures recorded in Beilstein's "Handbuch" were determined by observing the behavior of the acids when heated in melting-point tubes. There is no claim for exactness.

Summary

1. The temperatures have been determined at which malonic acid and certain of its alkyl derivatives break down into carbon dioxide and monobasic acids.

2. The influence of the radicals studied on the decomposition temperatures is of the same order of magnitude as that found in the earlier study of the pyrolysis of triphenylmethyl-alkyl ethers; the temperature is lowered in the two series as the radical is changed from methyl to ethyl to *n*-propyl but rises when *n*-butyl is present. The isopropyl radical derivatives in the two series decompose at lower temperatures than the *n*-propyl compounds.

3. In both series of compounds the decomposition temperatures fall in the same order, with varying alkyl radicals, as the rates at which alcohols containing the same radicals react with an acyl chloride. There appears to be a relationship between the effect of a radical on the lability of a bond as measured by the temperature of pyrolysis and the rate at which the bond is broken in a chemical reaction.

Cambridge, Massachusetts