Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.0; H, 6.3. Found: C, 75.2; H, 6.2.

Since the methoxyl compound is not affected by strong alkali it was possible to determine the relative amounts of C and O alkylates with sufficient accuracy by dissolving the entire product of the reaction in ether, extracting the ethereal solutions with successive portions of 40% aqueous potassium hydroxide until the extracts remained colorless, removing the ether and then distilling the methoxyl compound in a high vacuum. It boiled at 180–185° (0.05 mm.) and melted at 32°. The relative amounts of methoxyl compound obtained by various methods of alkylation were as follows: the reaction between the sodium salt and dimethyl sulfate in acetone gave 80.9% and in ether 64.2%. The reaction between the same salt and methyl iodide gave in acetone 64.6% and in methyl alcohol 50.9%. The potassium salt treated with dimethyl sulfate in water gave 57.1% but owing to experimental difficulties this value is not as accurate as the others.

Coupling, $C_6H\ COCOCH(C_6H_5)CH(C_6H_5)COCOC_6H_5$.—A suspension of the sodium salt in ether was treated with the calculated quantity of iodine and left to itself until all the yellow salt had disappeared. The mixture was then washed with thiosulfate and water, and the ethereal layer was dried and concentrated. It deposited a yellow solid which after recrystallization from ether, in which it is sparingly soluble, melted at 198°. The yield was small.

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.7; H, 5.0. Found: C, 80.8; H, 5.1.

In order to prove the structure of the tetraketone 0.2 g. of the substance was suspended in an alkaline solution of hydrogen peroxide. The solid gradually dissolved and the solution became colorless. On acidification it deposited a mixture of acids that could be separated by distillation with steam. The distillate contained benzoic acid and the residue deposited a solid acid which crystallized from ether in needles and which melted at 229°—the melting point of diphenylsuccinic acid. The identification was completed by converting the acid into the silver salt and this in turn into the ethyl ester. The ester melted at 135°.

Reaction with Phenylmagnesium Bromide, $C_6H_5CH_2COC(C_6H_5)_2OH$.—An ethereal solution of 10 g. of the diketone was added to phenylmagnesium bromide prepared from 5.5 g. of magnesium. The product of the reaction, isolated in the usual manner, crystallized from ether–petroleum ether in colorless needles and melted at 60°. The yield was 89%.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 82.0; H, 6.0. Found: C, 81.8; H, 6.0.

The position of the entering phenyl group was established by oxidation with chromic acid in glacial acetic acid; the products were benzophenone, phenyl acetic acid and a trace of benzoic acid. When added to a standard solution of methylmagnesium iodide the substance rapidly liberated one mole of gas in the cold and a second mole slowly on heating. Two moles of reagent were consumed; the substance therefore enolizes more readily than it combines with a second mole of the reagent.

Summary

This paper contains a description of the most conspicuous properties of benzyl phenyl diketone—the extent to which it is enolized under various conditions, its autoxidation and the manner in which it is alkylated and acylated.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 21, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. V. The Strength of Bonds in Organic Molecules

BY F. O. RICE AND WILLIAM R. JOHNSTON[1]

In order to develop a theory of the thermal decomposition of organic compounds through a free radical mechanism[2] it is necessary to know the activation energies of the various processes occurring during the different stages of the decomposition. In general, according to the theory, these elementary processes may be divided into three classes: (1) the primary unimolecular dissociation of the original compound into two free radicals through rupture of a bond; (2) the decomposition of a large free radical which may be thus formed into one or more unsaturated compounds and a smaller free radical or a hydrogen atom; (3) the reactions of the free radicals with the surrounding molecules of the original substance. In this paper we will report some measurements which we believe give the activation energy of the primary process for a number of different compounds.

Since most compounds appear to decompose homogeneously and according to a unimolecular law, and since this decomposition seems to involve a primary splitting of the molecule into two fragments, we can approximate the strength of the bond which breaks by ascertaining the activation energy involved in this decomposition proc-

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(1) Fleischmann Company Fellow, 1930–1933.

(2) Rice, THIS JOURNAL, **53**, 1959 (1931); **55**, 3035 (1933).

ess. The activation energy plus the average energy of the molecules at the temperature of decomposition gives an approximate measure of the strength of the linkage which breaks. This energy sum constitutes all of the available molecular energy and must therefore constitute at least an upper limit for the strength of the bond involved in the primary decomposition.

The method used is the same as that already described in earlier papers for experiments with acetone[3] and with ethane.[4] The organic compound is passed rapidly through a quartz tube at low pressures (0.2–2 mm.), and is heated by means of an electric furnace to a temperature at which it decomposes slightly. Standard mirrors of antimony are placed at varying distances from the end of the furnace. The time required to remove a mirror is evidently inversely proportional to the concentration of the free radicals at that point.[5] The time of removal of a mirror at the end of the furnace can be found by extrapolation; for small fractional decompositions we may assume that the concentration of radicals at the end of the furnace is proportional to the rate of dissociation of the organic compound. If, therefore, we perform the experiment at two or more furnace temperatures, we can determine the activation energy of the primary dissociation into free radicals, and thus the strength of the bond which undergoes the primary rupture.

Various objections may, of course, be urged against this method of determining the activation energy. In the first place, the radicals originally formed undoubtedly decompose further, and the activation energy of this secondary process must be simultaneously measured. In the second place, the free radicals may react with the surrounding molecules of the original substance and in this way start a chain reaction; and, third, since the organic vapor passes through the furnace in about $^1/_{1000}$ of a second, there is a question whether it reaches the temperature registered by the thermocouple.

Regarding the first of these objections it would seem that all free radicals except methyl are intrinsically unstable as compared with organic molecules; this is because their decomposition into an unsaturated compound and a smaller free radical is coupled with double bond formation. Since, therefore, the decomposition of an organic radical probably has an activation energy 40–60 Cal. lower than that of the compound from which it was formed, it cannot have any detectable effect on our measurements of the primary activation energy.

The second difficulty may arise when a chain reaction occurs, because the chain length may not be the same at both temperatures and consequently we would not be measuring the temperature coefficient of the primary reaction. A simple calculation, however, shows that this difficulty does not arise. Under our conditions a fragment undergoes 3000–7000 collisions during its passage through the furnace; if the activation energy of the reaction between the fragment and the surrounding molecules were 20 Cal., there would be no chain reaction, because $\epsilon^{-20,000/2400} \sim 10^4$ collisions would be required for each reaction at 900°. If, however, the activation energy of the reaction of the fragment with the surrounding molecules were only 10 Cal., a chain reaction would occur, because reaction between the fragment and the surrounding molecules would take place at about every hundredth collision at 900°. This, however, would have no effect on the experimental measurement if the chain termination within the furnace is negligible, because each reaction of the fragment with one of the surrounding molecules results in the formation of an unsaturated molecule and another fragment.

The third difficulty, namely, the attainment of temperature equilibrium, is more serious and we attempted to obtain experimental evidence regarding this point by investigating the effect (1) of changing the diameter and length of the furnace, (2) of changing the rate of flow of gas through the furnace, (3) of different temperature intervals, on the activation energy. A preheating furnace was fitted to the quartz tube immediately in front of the main furnace, thus doubling the heated length of the tube; a series of experiments was then made in which the preheater was held at various temperatures, finally also at the temperature of the main furnace. Experiments were further performed using different pressure gradients in the tube, and also with tubes of different internal diameter. The results obtained in all these experiments showed a maximum variation of about ±3 Cal., which is less than the experimental error. Finally, we found that plotting $1/T$ against log k

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(3) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932).

(4) Rice and Dooley, *ibid.*, **55**, 4245 (1933).

(5) Separate experiments showed that the time of removal of an antimony mirror is not appreciably affected by the temperature of the mirror up to about 300°.

(measured by the time of mirror disappearance) gave a straight line over a range of 150°. These experimental results seem to afford strong evidence that the gases really attained the furnace temperature in all these experiments.

On the other hand, the fact that a molecule makes only a few thousand collisions during its passage through the furnace makes it appear improbable that the temperature registered by the thermocouple was really attained by the molecules even at the instant of leaving the furnace. It seemed therefore very desirable to make a theoretical study of the temperature distribution of gases flowing through tubes at low pressures and Professor Herzfeld has recently published[6] a theoretical investigation of this problem.

He has shown that the flow of gas is laminar under all conditions obtaining in our experiments; furthermore, two cases must be considered; first, when the pressure drop is less than 0.003 mm. per cm., and, second, when the pressure drop is greater than 0.03 mm. per cm. In the first case temperature equilibrium is reached throughout the body of the gas, and under the conditions of our experiments the gas comes within 1% of the wall temperature in less time than is required for its passage through a furnace 3.5 cm. long.

On the other hand, in some of our experiments the pressure gradient was greater than 0.03 mm. per cm.; the calculations show that in this case the velocity is far too great to allow the attainment of equilibrium over the whole cross-section. Under these conditions it was found that only in a thin layer of gas next to the walls does the number of radicals correspond to the temperature of the walls; the core is relatively cold and contains a negligible number of radicals. However, because of the form of the Arrhenius equation, with the rapid decrease of activated particles with falling temperature, only the highest temperature is of significance. At the end of the furnace there will be a diffusion of molecules and radicals from the hot layer next to the wall and of molecules from the relatively cold core. The latter act only as diluents and the amount of dilution is nearly independent of the temperature of the furnace. Accordingly, the temperature coefficient of the concentration of radicals at the standard mirror is very little affected by the fact that in some cases the radicals come from only a small fraction of the gas.

Herzfeld has pointed out that his calculations refer only to heat transfer to translational and rotational degrees of freedom; if the heat transfer from translational to vibrational degrees of freedom is equally fast, the length of furnace (3.5 cm.) necessary to attain equilibrium in these experiments will be somewhat increased. On the other hand, if, as is probable, the heat transfer to the molecular bonds is slow, the temperature coefficient of the free radical concentration will not be affected providing the rate of transfer of kinetic to internal energy is independent of the temperature or nearly so. This problem has not yet been investigated.

In view, therefore, of the results of this theoretical investigation, together with the fact that changing the diameter and length of the furnace and the temperature interval over which the measurements are made does not alter the temperature coefficient, we may assume with some degree of confidence that we are measuring by this method the activation energy of the simple primary rupture of organic molecules into two free radicals.

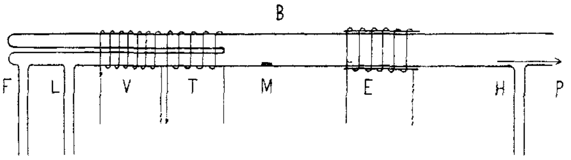

Fig. 1.—Apparatus for measuring the temperature coefficient of the dissociation of organic compounds into free radicals.

Experimental

The experimental arrangement is shown in Fig. 1. The organic compound to be investigated is placed in a small Pyrex flask (not shown in the sketch), which is connected through a ground glass joint and capillary tubing to a quartz tube B one centimeter in diameter. The quartz tube is the reaction tube and is covered for about twenty centimeters by an electrically heated furnace VT. The reaction tube is connected at P to a trap which is attached to a Gaede three-stage mercury vapor pump backed by an oil pump. The organic vapors are pumped through the reaction tube at rates of about 10–20 meters per second. The vapors are partially condensed in the trap by using solid carbon dioxide, thus increasing the pumping speed. The vapor source is maintained at constant temperature by a suitable bath of ice or solid carbon dioxide. The pressures are measured at the two side-arms L and H which are connected with a McLeod gage. The furnace temperatures are measured by means of a double junction platinum–platinum + 10% rhodium thermocouple. The furnace actually consists of two parts—a preheater and a cracking furnace. The preheater was always kept at approximately 150° below the cracking furnace.

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(6) Herzfeld, *Physics*, **4**, 362 (1933).

In operation, the organic vapors are admitted to the previously evacuated system by opening a stopcock. They first enter the quartz side-arm F, which is connected with the reaction tube by means of capillary tubing; by regulating the length and diameter of this tubing according to the particular compound being investigated the pressure at the furnace could be kept at a few tenths of a millimeter. The free radicals produced are observed at various distances from the furnace by placing standard metallic mirrors on the walls of the tube. The mirrors of antimony are made standard by careful heating of an antimony pellet M with a small cylindrical Pyrex glass furnace E which was movable along the quartz tube. Each mirror was carefully cooled by a jet of air. It was found that standard mirrors could be best obtained by heating until the mirror just begins to form and then removing the heater. By using the air jet the antimony could be condensed in a sharply outlined film about 4–7 mm. in width. The antimony pellet contained an iron core and could be moved by a magnet to various positions in the tube.

As mentioned previously, the time required for the free radicals to remove a given standard mirror is taken as an arbitrary measure of the concentration of the free radicals at that point. We determined the concentration of the free radicals at various distances from the furnace—from ten to thirty millimeters; plotting time of removal against distance from the furnace we obtained an approximately straight line and extrapolation of this gave an estimate of the time of removal of a standard mirror at the end of the furnace. This time of removal at the furnace is evidently inversely proportional to the concentration of free radicals at the furnace. The free radical concentration should be a maximum at the end of the furnace and should be proportional to the rate at which the organic compound cracks. By determining removal times at the furnace for different temperatures one can get a measure of the velocity constant of the decomposition reaction at different temperatures and hence the temperature coefficient and activation energy.

In all the experiments described in this paper a quartz tube approximately 1 cm. in internal diameter was used. The results obtained for acetone and heptane checked with other results obtained using furnaces of 0.6 and 1.3 cm. internal diameter. The different compounds were the best grade obtainable commercially and were used without further purification. In the case of acetone and heptane very pure samples were available in addition to the commercial samples but no difference could be detected.

The standard mirrors were prepared in the same way throughout the experiments so that they all contained the same amount of metal (antimony). By varying the pressure in the furnace according to the particular compound used we were able to make the measurements over approximately the same temperature range for the different organic compounds.

A. Experiments with Dimethyl Carbonate.—As an example of the experimental work the data on dimethyl carbonate will be presented in some detail.

Table I gives measurements of the time required to remove antimony mirrors at various distances from the end of the cracking furnace, which was kept at 1152°K. Since the time near the furnace is most important, great care was taken to determine the removal time at the one centimeter distance. It was not possible to form standard mirrors much closer to the furnace than one centimeter since the heat of the furnace precluded sufficient cooling.

TABLE I

DIMETHYL CARBONATE

Temp. at furnace, 1152°K. (879°C.). Press. at furnace, 0.24 mm.; press. gradient 0.0024 mm./cm.

Dist. from furnace, cm.	Removal times of standard mirrors, sec.							Average
1	4.4	4.0	4.4	6.6	4.2	4.5	4.3	4.3
1.2	5.0	5.4	5.1	5.0	4.8	5.3		5.1
1.4	5.0	5.4	4.9	5.2	5.4			5.2
1.5	5.7	5.4	6.0	5.9	5.6			5.7
1.8	6.8	6.4	6.9	6.3				6.6
2.0	7.2	6.8	7.4	7.0	6.6			7.0
2.4	8.4	7.8	7.6	8.2	8.0			8.0
1.0	4.2	4.4	4.2	4.5	4.4	4.2	4.0	4.2
1.0	4.5	4.4	4.0	4.2	4.3			4.3
0 (Extrapolated)								1.85

These measurements, using the same standard mirrors, were repeated at different temperatures. Table II gives the results of measurements for the various temperatures.

TABLE II

DECOMPOSITION OF DIMETHYL CARBONATE AT DIFFERENT TEMPERATURES

Press. at furnace, 0.24 mm. Press. gradient, 0.002–0.0024 mm./cm.

Temp., °K. . 1043		1080		1152		1188	
Temp., °C. . . 770		807		879		915	
Dist., cm.	Av. time, sec.	Dist., cm.	Av. time, sec.	Dist., cm.	Av. time, sec.	Dist., cm.	Av. time, sec.
1.0	70.3	1.0	22.5	1.0	4.3	1.0	2.2
1.2	74.5	1.2	24.0	1.2	5.1	1.2	2.3
1.3	77.3	1.3	24.3	1.4	5.2	1.3	2.6
1.5	80.6	1.5	25.6	1.5	5.7	1.4	2.8
1.7	88.5	1.7	27.8	1.6	5.6	1.5	3.2
1.9	88.2	1.8	27.2	1.8	6.6	1.7	3.0
2.0	92.7	2.0	28.0	2.0	7.0	2.0	3.6
2.5	99.6	2.4	32.0	2.4	8.0	2.5	4.5
0	47.5	0	16.0	0	1.85	0	0.55

The last line contains the extrapolated times of disappearance of the standard mirrors at the end of the furnace.

Only the mean times are given but in every case these were obtained from several measurements as illustrated in Table I. In all cases the pressure at the furnace was essentially the same and the pressure gradient remained between 0.0020 and 0.0024 mm. per cm. length. As the temperature was increased, the temperature of the preheater was also raised so that it was always kept approximately 150° below the cracking temperature.

Assuming that the times at the furnace are, quite reasonably, inversely proportional to the specific reaction constant at the corresponding temperature, they may be substituted for "*k*" in the usual Arrhenius plot. To obtain the activation energy the log of "*k*" was plotted against $1/T$, the reciprocal of the absolute temperature. The slope of the straight line when multiplied by $2.303\ R$, where R is the gas constant, gives the activation energy. The plotted data are shown in Fig. 2, Curve II.

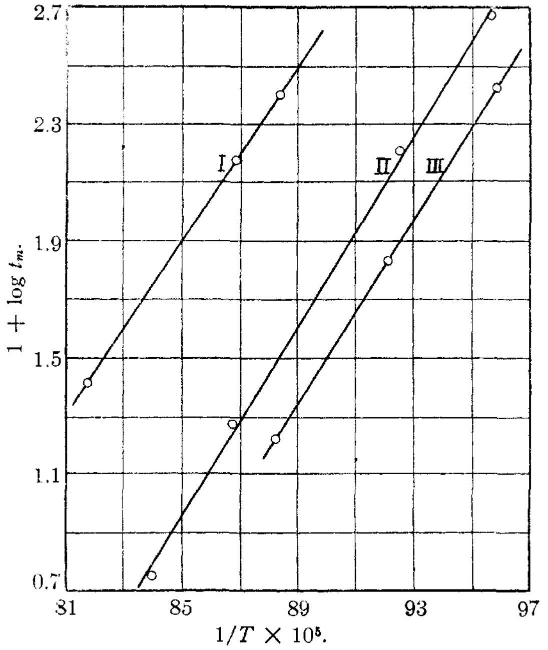

Fig. 2.—Temperature coefficient of the dissociation of organic compounds into free radicals: I, ethyl alcohol; II, ethyl carbonate, 10-cm. furnace; III, ethyl carbonate, 20 cm. furnace.

In order to be certain that the organic vapor was reaching the temperature measured, the temperature of the preheating furnace was raised to that of the main furnace, that is, in effect doubling the length of the cracking furnace. The pressure at the furnace was kept the same and the gradient changed from 0.0019 mm./cm. to 0.0023 mm./cm. over the temperature range studied. The results of this experiment are shown in Table III. By plotting the results as before we obtained an activation energy of 72.5 Cal. as compared with 74.2 Cal. with a furnace only one-half as long; this variation is within our experimental error.

TABLE III

DECOMPOSITION OF DIMETHYL CARBONATE AT DIFFERENT TEMPERATURES USING FURNACE 20 CM. LONG

Press. at furnace, 0.24 mm. Press. gradient, 0.002–0.0024 mm./cm.

Temp., °K......1043		1088		1134	
Temp., °C......770		815		861	
Dist., cm.	Av. time, sec.	Dist., cm.	Av. time, sec.	Dist., cm.	Av. time, sec.
1.0	43.3	1.0	11.9	1.0	5.9
1.2		1.2	12.9	1.2	6.4
1.3	46.1	1.3	14.0	1.3	7.6
1.4	51.0	1.5	15.2	1.4	7.5
1.5	50.2	1.8	16.2	1.5	8.2
2.0	62.3	2.0	18.4	2.0	10.5
2.2	62.3	2.2	20.0	2.2	11.0
0	26.0	0	6.0	0	1.6

In another experiment the temperature of the preheater was varied over a wide range while the temperature of the cracking furnace was kept constant at 770°. The time of removal of a standard mirror was measured at a distance of 1 cm. from the furnace. It was found that the time of removal of the mirror did not change appreciably until both furnaces were brought to the same temperature, thus indicating that over a considerable range the preheater possessed about the same efficiency in promoting accurate temperature control. In accordance with these results the preheater was kept about 150° below the cracking furnace in all the subsequent experiments, unless otherwise stated, so that it could act effectively and yet not cause additional cracking. The data are presented in Table IV.

TABLE IV

DIMETHYL CARBONATE, EFFECT OF VARYING TEMPERATURE OF PREHEATING FURNACE

Temp. of main furnace, 770°; dist. of standard mirror, 1 cm.

Temp. of preheating furnace, °C.	580	627	655	737	770	770
Time of removal of mirror, sec.	73.7	68.6	70.4	68.3	47.0	46.9

B. Experiments with Other Organic Compounds.—The method has been described in detail for dimethyl carbonate. The data have been obtained in the same way for other compounds. In all cases the standard mirrors were prepared in the same way and of about the same thickness. It was necessary to vary the pressures at the furnace somewhat in order to regulate the concentration of free radicals produced. Approximately the same temperature range was used and approximately the same concentration of radicals was present. Since the conditions were kept relatively the same, it is reasonable to expect that the relative errors are not as large as the absolute errors and are probably around 5%.

The data obtained for nine other compounds are summarized in Table V; the data for dimethyl carbonate and ethane are also included in this table.

TABLE V

Compound	Press. at furnace, mm.	Press. gradient, mm./cm.	Furnace temps., °K.				t_m				E
Ethane			1179	1233							79.5
Dimethyl carbonate	0.24	0.0022	1043	1080	1152	1188	47.5	16.0	1.85	0.55	74.2
Propane	1.67	.012	1010	1080	1152		32.2	3.3	0.39		71.5
n-Butane	1.65	.010	1010	1080	1152		18.9	2.3	.35		65.4
n-Pentane	1.54	.0099	996	1033	1052	1080	36.0	12.0	6.9	3.0	64.0
n-Heptane	0.25	.003	1010	1080			2.0	0.25			63.2
Acetone	.84	.009	1010	1080	1134		19.6	2.0	0.40		70.9
Acetaldehyde	.88	.0092	1116	1152	1179		24.0	9.0	4.5		69.4
Ethyl alcohol	(2.0)	.02	1134	1152	1223		24.0	14.4	2.5		68.6
Diethyl ether	0.37	.0043	1010	1080	1152		28.8	3.4	0.40		68.6
Dimethyl ether	.80	.0087	1080	1152	1188		16.4	1.75	.50		81.1
Ethylene oxide	.22	.0026	1052	1088	1134	1188	14.0	7.0	3.0	1.3	44.0
Trimethylamine	.32	.0038	953	1010	1080		30.0	6.202	1.35		50.8
Dimethylamine	.13	.0011	1080	1116	1152	1188	22.8	11.2	5.0	2.5	52.0

The furnace temperatures are given in the fourth column and in the fifth column (t_m) are found the corresponding values for the removal times of standard mirrors at the end of the furnace. These removal times are extrapolated values from a number of mean values obtained in exactly the same way as described in the case of methyl carbonate. The sixth column contains the activation energy obtained by plotting t_m against the reciprocal of the absolute temperature.

Summary

We have measured the activation energy of the decomposition of a number of organic compounds into free radicals. This has been done by passing the compounds rapidly, at low pressures, through a furnace heated to different measured temperatures; the extent of the decomposition into free radicals was determined by means of the Paneth effect on metallic mirrors.

The ethereal C–O bond is stronger than the C–C bond as shown by the activation energies for dimethyl ether, ethane and propane which are, respectively, 81.1, 79.5 and 71.5 Cal. The C–N bond is relatively weak, since the activation energy of trimethylamine is only 50.8; the three membered ring compound ethylene oxide is the least stable compound examined and decomposes with an activation energy of only 44.0 Cal. There seems to be a definite diminution in stability as one passes from the lower to the higher members of a homologous series.

BALTIMORE, MD. RECEIVED SEPTEMBER 22, 1933