

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Explosion of Ethyl Azide¹

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1. Introduction

Recent work of Allen and Rice² indicates that the explosion of azomethane is a purely thermal explosion, that is, it is due to the self-heating of the gas from the energy liberated during the decomposition of azomethane, uncomplicated by any effects due to branching chains. Since the quiet decomposition of ethyl azide³ is in many respects similar to that of azomethane, and since the decomposition of ethyl azide is undoubtedly strongly exothermic, it seemed reasonable to expect that the ethyl azide explosion would also be a thermal explosion. As unambiguous examples of thermal explosions are very rare, we have accordingly studied the explosion of ethyl azide, and have, indeed, found that the expectation that it, too, would be a thermal explosion, is fairly definitely confirmed.

It may be well to remark, however, that the evidence against the possibility of the ethyl azide decomposition being a chain reaction is by no means as convincing as in the case of azomethane, nor does the fact that the explosion is apparently a purely thermal one offer any further evidence against this possibility. A chain explosion depends upon the possibility of the chain branching, and if the chain cannot branch then the only kind of explosion possible is a thermal explosion. A thermal explosion depends upon the acceleration of the reaction rate by the self-heating of the gas, and the self-heating may in general be expected to have precisely the same effect upon a non-branching chain reaction as upon a reaction in which no chain is involved.

2. Experimental Part

The experimental procedure was very similar to that used by Allen and Rice in the study of the azomethane explosion. The ethyl azide vapor (or in some cases a mixture of ethyl azide and an inert gas) was introduced at known pressures into an evacuated bulb which was in a furnace whose temperature could be controlled to about $\pm 0.3^\circ$. At each temperature there was a critical pressure, which could be determined within about 1 mm., above which an explosion would occur after a certain induction period and below which no explosion would

take place. When no explosion occurred the rate of decomposition was measured. For further details regarding the experimental procedure the reader may be referred to the paper of Allen and Rice.

Preparation of Material.—Ethyl azide was prepared by the method of Staudinger and Hauser⁴ from sodium azide and fresh ethyl sulfate, the ethyl azide being distilled from the mixture through a calcium chloride tube. It was fractionated three times, and a sample boiling from 48.5 to 49.5° was collected in a trap which could be sealed to the high vacuum line. The various preparations always boiled over a range of about 2°. The fraction in the trap was chilled with dry ice and acetone, and the trap evacuated. The sample was freed of dissolved gases by pumping out when well chilled, allowing to warm up, and repeating several times.

Altogether ten different samples of ethyl azide were prepared, and some little difficulty was encountered in getting perfectly pure azide. The determination of the critical explosion pressure to within less than a millimeter would appear, indeed, to be a rather exacting test of the purity of the preparation. The explosion limits of the various samples and different fractions of the same sample would sometimes differ from each other by 10%. (One sample, No. 4, gave some results off by as much as 20%.) A deviation of 10% in the explosion limits would indicate an impurity of about 10% in the sample having the higher explosion limit, provided the impurity is an inert gas, since the critical partial pressure of azide would be expected to be approximately unchanged with this amount of inert gas present. This is a rather large amount of impurity, and the fact that systematic deviations between different samples, of this order of magnitude, were obtained leads us to believe that the impurity, whatever it is (possibly alcohol or ether) must form an approximately constant boiling mixture with the azide.

Sample No. 10, the last one prepared, in addition to being purified as noted above, was shaken for a half hour with calcium chloride, and it apparently was the best sample prepared, as the various fractions boiling from 48.0 to 48.5°, from 48.5 to 49.25°, and from 49.25 to 49.75° showed no appreciable differences in the explosion limit. All other samples gave critical pressures which were either equal to these or higher by not more than 10%, except sample No. 4, which gave very erratic results. Most of the results, including the experiments with mixtures of the azide and inert gases, were obtained with Sample No. 8 which gave critical pressures close to those of Sample No. 10, in no instance more than 5% higher. The last portions of Sample No. 8 agreed better with Sample No. 10 than the first portions used.

Helium and carbon dioxide were used in various experiments as inert diluents. The helium was taken from a tank and purified by passing it in turn over hot copper (prepared by reducing copper oxide with hydrogen), hot

(1) Presented in part at the Florida meeting of the American Chemical Society, March, 1934.

(2) Allen and O. K. Rice, *THIS JOURNAL*, **57**, 310 (1935).

(3) Leermakers, *ibid.*, **55**, 2719 (1933).

(4) Staudinger and Hauser, *Helv. Chim. Acta*, **4**, 872 (1921).

copper oxide and calcium chloride. The carbon dioxide was prepared by carefully heating sodium bicarbonate, measuring the flow with a small sulfuric acid bubble counter. The gas was finally dried with calcium chloride.

The effect of adding a small amount of air to the azide was also tested, as air is a possible impurity. It was found that 11% of air lowered the explosion limit by 8% at 280°, from which it may be inferred that no appreciable error could be caused by failure to free the azide from the last traces of air.

3. Results on Explosion Limits

In Table I we have summarized the main results on the explosion limits. These explosion limits were obtained, as in the work of Allen and Rice, by making a series of trials, holding the furnace at as nearly constant a temperature as possible, and gradually closing in on the explosion limit. The explosion limit is taken as the mean between the highest pressure at which the gas did not explode and the lowest pressure at which it did explode. The column marked "Dev." gives the difference in pressure between the

TABLE I
EXPLOSION LIMITS IN 200-CC. BULB

Temp., °C.	Critical pressure, mm.	Dev.
	100% Ethyl Azide	
258.5	105.2	0.5 (b)
259.9	91.7	1.3 (b)
263.0	64.6	1.1 (b)
265.2	59.1	0.6
265.2	55.9	.4
265.0	55.0	.5
265.1	52.7	.7 (b)
269.7	37.8	1.0 (a)
269.9	36.6	0.2 (a)
270.0	36.4	.4
270.3	34.9	.3
270.0	33.5	.7 (b)
274.5	25.1	.4
279.8	17.4	(a)
280.0	17.0	.3
280.0	16.7	.3
280.0	15.9	.9 (a)
280.0	15.9	.6 (b)
285.1	11.6	.5
289.8	10.0	.5 (a)
289.9	10.0	(a)
289.7	9.8	.3
289.9	9.7	.4
290.0	9.3	.3 (b)
289.7	8.8	.4
295.1	6.9	.5
299.9	5.9	.4
299.9	5.6	.6 (b)
300.0	5.6	.2 (a)
310.4	4.0	.5 (b)
320.2	3.1	.4 (b)

67% Azide, 33% Helium

266	66	
270.0	45.3	0.4
274.6	31.8	.6
280.1	20.9	.4
285.0	16.1	.6
290.0	12.0	.1
295.2	8.7	.5
299.5	7.3	.3
305.4	5.7	.2
310.1	4.5	.5

50% Azide, 50% Helium

269	58	
270.5	51.6	0.2
274.3	38.2	1.3
274.9	37.0	0.8
279.9	25.6	.7
285.1	18.9	.4
289.9	14.4	.2
289.7	14.0	.4
299.9	9.1	.3

50% Azide, 50% Carbon Dioxide

269.8	36.8	0.2 (a)
280.0	17.8	.3 (a)
289.8	9.7	.2 (a)

^a 5th azide. ^b Last quarter of 8th azide.

tabulated explosion limit and the highest non-explosive or lowest explosive run, except in a few cases in which the temperature varied sufficiently so that the lowest explosion occurred at a lower pressure than the highest quiet decomposition. For the most part, however, the temperature did not vary more than half a degree for the lowest explosion and for the highest quiet decomposition, and the mean of these temperatures is tabulated.

Table I includes all the experiments made in the 200-cc. bulb with azide samples 5 and 8. Except where otherwise indicated the results refer to Sample 8. Explosion limits made with the last (highest boiling) quarter of this azide are specially marked. These appear to have slightly lower explosion limits than the others. It might be supposed that this is an indication that this fraction is actually purer, containing less inert material, than the others. The low boiling fraction, however, appeared also to give slightly lower explosion limits, though in this case the difference was so slight that it did not appear worth while to distinguish these experiments from the others.

The results are exhibited graphically in Fig. 1.

According to the theory of thermal explosions⁵

(5) Semenov, *Z. Physik*, **48**, 571 (1928); Allen and Rice, *Ref. 2*, p. 313.

if one plots $\log (AP^*/A_\infty T_0^3)$ against $1/T_0$, as in Fig. 2, a straight line of slope $E/2.3R$ should be obtained. Here P^* is the critical explosion pressure when the bulb is held at the temperature T_0 , E is the energy of activation of the quiet thermal decomposition, R is the gas constant,

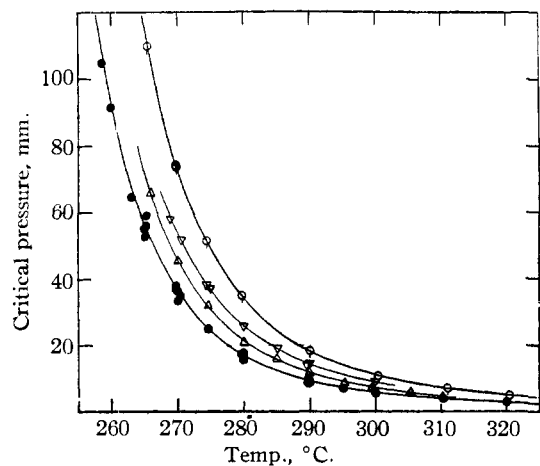


Fig. 1.—Explosion limits; ●, pure azide, 200-cc. bulb; ○, pure azide, 50-cc. bulb; △, 33% He; ▽, 50% He.

A is the temperature independent factor of the rate constant for the pressure P^* , and A_∞ is the corresponding quantity for infinite pressure, the factor A/A_∞ thus correcting for the falling off in rate of the unimolecular reaction at low pressures. This quantity we have estimated by extrapolation from the curves given by Leermakers.⁶ In the case of the mixtures we have assumed that the added gases do not activate ethyl azide and thus have considered the partial pressure of azide in calculating A/A_∞ . This is undoubtedly very nearly correct when helium is the inert gas, but is more questionable with carbon dioxide. However, at worst, the error caused in this way cannot be very great.

The straight line in Fig. 2 indicates the theoretical slope, E being taken as 39,000 calories per mole from rate measurements, which will be discussed subsequently. It will be seen that the agreement between experiment and theory is very good over the higher part of the temperature range, which corresponds to the lower part of the pressure range. At low temperatures and high pressures, however, deviations begin, and the critical pressure is nearly two-fold higher than expected at the lowest temperature used. This is similar to the deviations observed by Allen and Rice in the case of azomethane, but it is

(6) Leermakers, Ref. 3, Fig. 2.

more marked and sets in at a lower pressure. This we believe to be due to the quantity x , which gives the rate (per unit temperature rise of the gas in the flask and per unit surface area) at which heat is removed from the reaction vessel, not being strictly constant but increasing with the pressure. The most puzzling feature is the fact that the deviation from constancy is so much more marked with ethyl azide than with azomethane.

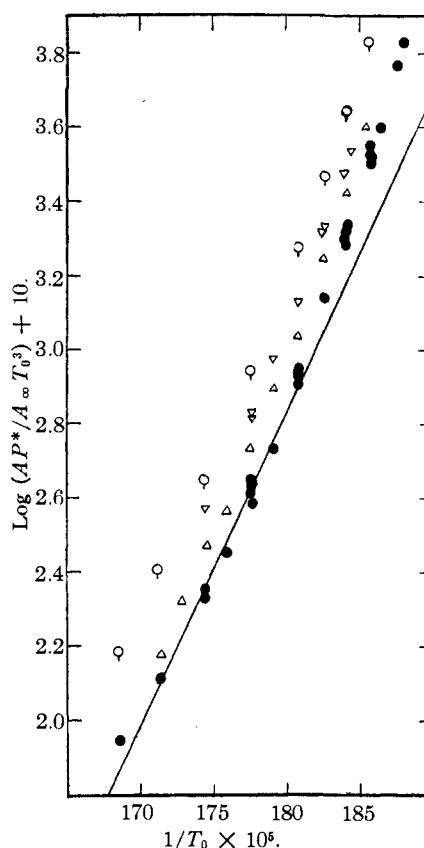


Fig. 2.—Explosion limits, with theoretical line: ●, pure azide, 200-cc. bulb; ○, pure azide, 50-cc. bulb; △, 33% He; ▽, 50% He.

The effects of helium and carbon dioxide on the explosion of ethyl azide resemble closely the effects of helium and nitrogen on azomethane. Helium increases the partial pressure of ethyl azide necessary for explosion, presumably because of an increase in x , due to the high heat conductivity of helium. Carbon dioxide has very little effect on the explosion limits. This behavior, and particularly the difference in the effects of the two gases, is not what one would expect if the explosion involved branching chains, as Allen and Rice have noted, and may be taken

as evidence that the explosion is a thermal explosion.^{6a} It will be noted from Fig. 2 that experimental points for the mixtures parallel the points for pure ethyl azide very closely, even where the deviation from the theoretical line occurs. Experiments on the explosion of ethyl azide in the presence of diethyl ether are now under way. Ether retards the explosion and changes the shape of the curve somewhat, and it is hoped that this study will throw further light on the nature of thermal explosions.

4. Effect of Size of the Reaction Vessel

If we assume x and A are constant, then, according to the theory, the critical pressure at any temperature should be proportional to the ratio of area of walls to the volume of the vessel. Therefore, if we change from a 200-cc. to a 50-cc. bulb, the critical pressures should be changed by a factor of approximately 1.59.

In Table II we present the results of a series of experiments performed with a 50-cc. bulb. It is seen that, as found also by Allen and Rice in the case of azomethane, the ratio is actually larger than 1.59. This must be due to a difference in x for the two bulbs, caused by differences in the convection and turbulence. (The change in A with the pressure produces an effect in the other direction.) In Table II we have listed the ratios of x for the 50-cc. and 200-cc. bulbs at the different temperatures, taking into account the effect of the pressure on A . These results

TABLE II
EXPLOSION LIMITS IN 50-CC. BULB

Temp., °C.	Critical pressure, P_{50}^*	Dev.	P_{200}^*	P_{50}^*/P_{200}^*	x_{10}/x_{200}
265.5	109.9	1.2	55.0	2.00	1.29
269.8	74.4	0.2	36.6	2.03	1.32
269.9	73.7	.5	36.2	2.04	1.32
274.2	51.4	.5	25.6	2.01	1.32
279.8	34.8	.7	17.2	2.02	1.34
290.0	18.4	.5	9.2	2.00	1.37
300.3	10.7	1.1	5.5	1.95	1.35
311.0	7.0	0.3	4.0	1.77	1.25
320.4	4.9	.8	3.1	1.59	1.10

(6a) The argument of Allen and Rice was based in part on the difference between the effects of the two gases. It is conceivable that a chain might be broken in the gas phase by a process requiring a third body. If helium were an efficient and carbon dioxide a very inefficient third body, the difference might be explained in this way. Since, however, we have a lower limit of pressure for explosion, the chain-branching step would then presumably have to be a reaction of higher order than the third, which seems improbable. (It is, of course, not possible to distinguish by means of inert gases between thermal explosions and explosions which are partly thermal, such as the "degenerate explosions" of Semenov, "Chemical Kinetics and Chain Reactions," Oxford, 1935.)

resemble the results with azomethane in that x_{50}/x_{200} is greater than 1. The value of x_{50}/x_{200} appears, however, to be much more constant in the present work, and does not increase at the higher pressures as was found to be the case with azomethane. These differences may not be significant, however, in view of the small number of experiments made with azomethane.

5. Reaction Rates in Non-Explosive Runs

When an explosion did not occur the rate of the quiet decomposition was generally measured. Far too many sets of rate constants were thus obtained, to consider in their entirety. We shall, therefore, confine ourselves to a discussion of the rate constants obtained with pure azide, sample No. 8, in the 200-cc. bulb, and in the temperature range from 220 to 280°. While earlier runs were often more erratic than these, there was no noticeable systematic difference in the values of the rate constants. This is true also of runs done in the 50-cc. bulb and in the presence of inert gases. At temperatures above 280° the rates were so fast that the data were of little value. The experiments at lower temperatures were done in order to check our temperature scale with that of Leermakers, and satisfactory agreement was found.

TABLE III
DATA FOR TYPICAL REACTION RATE EXPERIMENTS

t , sec.	Run No. 375; temp., 220°	
	P , total, mm.	$k_0 \times 10^4$
0	131.9	
60	132.5	1.1
120	134.5	2.9
320	143	4.2
580	153	4.2
870	163	4.2
1200	173	4.3
1580	183	4.3
2040	193	4.3
t , sec.	Run No. 372; temp., 240°	
	P , total, mm.	$k_0 \times 10^4$
0	136.2	
30	139	0.8
65	147	2.2
114	157	2.2
230	167	2.1
285	177	2.5
420	197	2.5
680	216	1.9

The experiments were performed in the usual way, recording the time and the pressure at intervals during the run, and calculating the rate constants for the intervals. Data for some

typical experiments are presented in Table III. It will be observed that in each case the initial rate constant is low. Subsequent experiments in which air was admitted to the flask indicated that the cause of this was that pressure equilibrium had not yet been established at the time the stopcock was closed. Since the initial pressure was set equal to the pressure remaining in the storage bulb, and the true initial pressure in the reaction flask was actually slightly less than this, a considerable error was caused in the first rate constant, though the error was not great enough to affect appreciably the explosion limits. This error was greater than in the experiments of Allen and Rice because of the construction of the furnace, which was made larger in order to make it easier to control the temperature, thus necessitating a longer tube leading to the reaction flask. For the runs at the lower temperatures it was possible to estimate the true initial pressure by extrapolation from the first few readings to zero time. The rate constants finally used for the runs below 250° were calculated from the formula

$$k_0 = (t_2 - t_1)^{-1} \ln P_1/P_2 \quad (1)$$

where t_1 is the initial time, P_1 the initial pressure, t_2 the time of a reading near the point at which half the gas had decomposed, and P_2 the partial pressure of azide at time t_2 . In order to calculate the partial pressure of azide the ratio of the final pressure in the reaction flask to the initial pressure must be known. This ratio was found by Leermakers to be 1.81, and our results check his closely.⁷ When the run was allowed to go to completion, the experimental value for that run was used in calculating k_0 ; otherwise we used Leermakers' value.

The runs above 250° were corrected for the effect of the heating up of the gas on the rate of reaction. Allen and Rice have shown that, when this effect is taken into account, the rate of change of the partial pressure, P , of the reacting gas with the time, t , should be given by the equation

$$dt = - (ek_0)^{-1} (T_s^*/T_s) d(P/P^*) \quad (2)$$

where e is the base of natural logarithms, k_0 is the rate constant at the temperature T_0 of the flask, and where T_s , the actual steady state temperature of the gas, is a function of P given by the equation

$$(T_s/T_s^*)e^{1-T_s/T_s^*} = P/P^* \quad (3)$$

(7) In the explosive runs this ratio is higher, as expected on account of the high temperature attained during the explosion. It ranges from 2.94 to 3.04.

T_s^* being the value of T_s when $P = P^*$. From Equation (2) the value of the time at which the partial pressure has fallen to any definite value may be calculated, if k_0 is known, and compared with the experiments. In the case of azomethane Allen and Rice estimated k_0 by extrapolating the results of Ramsperger.⁸ In the present case, however, we have determined that value of k_0 which gives the best agreement with experiment. As these runs at higher temperatures were rather irregular, no attempt was made to get the correct initial pressure by extrapolation, but the observed values were used; this will cause but little error, however. A few typical calculations are given in Table IV. We give the calculated values of the time intervals " Δt , calcd.," corresponding to the observed change in pressure and to the value of k_0 listed for each experiment. These may be compared with the actual observed time intervals " Δt , obsd." For comparison, the values of k_0 calculated directly by the usual method for each interval are presented in Table IV. It will be noticed that in the runs at 260° these values exhibit a marked falling off in the rate constant as the run proceeds, similar to that observed in an analogous case by Allen and Rice; this is presumably due to the initial heating up of the gas and subsequent drop of temperature as the reaction proceeds. The results seem to be a little too irregular, however, to bring out very well the difference between runs close to the explosion limit and those somewhat further removed, and at higher temperatures this effect

TABLE IV
DATA AND CALCULATIONS FOR CERTAIN REACTION RATE EXPERIMENTS

In Runs 434, 435, 436, 444, which were done consecutively, slight variations in temperature occurred. The values of P^* are the best estimates we could make; that for Run 444 was determined at the time.

P , total, mm.	Δt , obsd., sec.	Δt , calcd., sec.	k_0 uncorr. $\times 10^2$
Run 434, $T_0 = 260^\circ$, $P^* = 88$, $k_0 = 0.00892$			
58			
61	10		0.64
67	12	12.0	1.18
73	11	14.7	1.50
79	22	18.2	0.89
85	24	23.4	1.03
91	36	22.0	0.90
99	76		.96
103	89		.85
105	90		.94
106.5	470		

(8) Ramsperger, THIS JOURNAL, 49, 912 (1927).

TABLE IV (Concluded)

P , total, mm.	Δt obsd., sec.	Δt calcd., sec.	k_0 uncorr. $\times 10^3$
Run 435, $T_0 = 260^\circ$, $P^* = 88$, $k_0 = 0.00850$			
74.2			
79	10		0.80
87	10	12.0	1.53
95	17	15.7	1.05
103	21	20.3	1.04
110	24	23.5	1.01
116	28	27.7	0.96
122	42	39.0	.87
126	38		.93
130	65		.84
134	180		.72
135.5	465		
Run 436, $T_0 = 260^\circ$, $P^* = 88$, $k_0 = 0.00822$			
87.3			
96	10		1.32
104	11	10.7	1.26
110	10	9.7	1.20
118	19	16.7	0.98
130	33	35.3	1.09
140	51	48.6	0.88
152	136		.85
156	185		.70
157.5	625		
Run 444, $T_0 = 260^\circ$, $P^* = 86.1$, $k_0 = 0.00889$			
85			
100	18		1.37
110	18	16.0	1.15
120	25	22.6	1.04
130	29	32.7	1.22
140	60	55.1	0.92
150	165		.80
152	105		.77
153.5	285		
153.6	195		
Run 380, $T_0 = 270^\circ$, $P^* = 34.2$, $k_0 = 0.0152$			
32.3			
39	13		2.2
47	27	25.1	1.9
51	20	21.9	2.0
55	28		2.3
58	86		1.4
59.3	216		
Run 383, $T_0 = 280^\circ$, $P^* = 16.5$, $k_0 = 0.0286$			
15.3			
19	12		3.0
24	26	26.0	3.5
26	34		2.6
27	33		3.8
27.4	110		

was not particularly noticeable; this is probably due to the greater errors inherent in the measuring of the more rapid rates, though the fast runs were not as irregular as those of Allen and Rice, and the peculiar effect of an apparent drop in the

rate constant with temperature at the highest temperatures, as reported by them, was not noticed here.

The values of k_0 , either as calculated from Eq. (1) or corrected for the increased temperature in the flask, were all corrected to infinite pressure by multiplying by A_∞/A , estimated as before by extrapolating from Leermakers' curves. The resulting values, k_∞ , are collected in Table V, and presented graphically, in the form of the usual Arrhenius plot, in Fig. 3. The straight line shown in Fig. 3 corresponds to an activation energy of 39,000 calories per mole. This agrees well with the value 39,740 reported by Leermakers. Although this agreement is very gratifying, it does not in itself prove that heating-up of the gas actually occurs, as we have found that the uncorrected points fall on nearly as good a straight line, with only a slightly different activation energy.

TABLE V
SUMMARY OF RATE MEASUREMENTS

T_0	P , mm.	$k_0 \times 10^3$, sec. ⁻¹	$k_0 A_\infty / A \times 10^3$
220.0	130.5	0.434	0.442
230.0	133.0	.973	.993
230.0	129.5	1.004	1.023
240.0	132.1	1.91	1.95
240.0	133.7	2.30	2.36
250.0	131.0	5.00	5.13
250.0	133.0	5.03	5.16
256.8	84.7	7.16	7.43
258.1	83.9	7.845	8.15
258.5	104.7	7.56	7.82
259.6	87.4	8.28	8.61
259.0	84.7	7.89	8.20
260.0	58.0	8.92	9.38
260.0	74.2	8.50	8.89
260.0	87.3	8.22	8.57
260.0	85.0	8.89	9.25
265.0	51.8	10.98	11.72
270.0	32.3	15.2	16.6
270.0	32.8	15.3	16.7
280.0	15.3	28.6	33.6
280.0	15.3	27.2	32.0

6. Direct Measurement of the Temperature of the Reacting Gas

We have seen in the above account that, in spite of differences between the two explosions the origin of which is not entirely clear, it seems most probable that the ethyl azide explosion like that of azomethane is a thermal one. Once again, however, it was deemed desirable to make a direct measurement of the warming up of the gas, when reacting just below the explosion limit,

by means of a thermocouple. For this purpose the same platinum-silver thermocouple used by Allen and Rice was remounted for use with ethyl azide.⁹ On performing the measurements we obtained the surprising result that the temperature rises recorded in the case of ethyl azide not only were far greater than those found with azomethane, but were 30-50% higher than would be expected from Eq. (3), though paralleling fairly well the rises predicted by that equation.

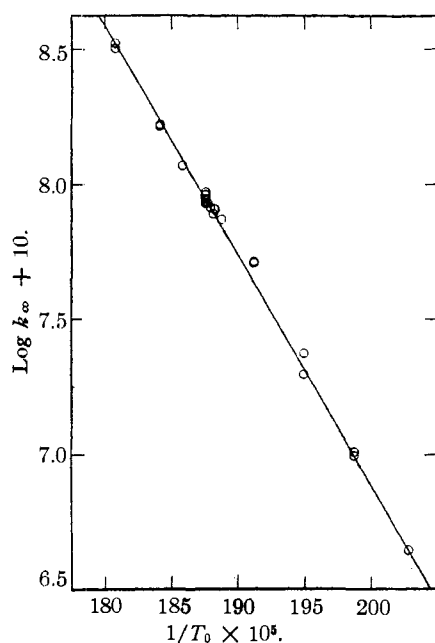


Fig. 3.—Reaction rates.

There are several possible explanations for this result. In the first place, the thermocouple junction was nearer the center of the flask in the experiments with ethyl azide, and this suggests the possibility that there is a considerable temperature gradient inside the flask, and that the

(9) An actual calibration of this thermocouple showed that it gave e. m. f.'s approximately 50% greater than those reported for platinum-silver thermocouples by Pelabon [*Ann. Phys.*, **13**, 169 (1920)]. The temperature rises reported by Allen and Rice should therefore presumably be lowered correspondingly.

temperature rise which enters into the theory is a sort of average temperature. Whether the explosion would be conditioned by an average temperature or the maximum temperature inside the flask would depend upon the exact mechanism by which heat is transferred inside the flask, and it is of course quite possible that the rate of transfer of heat to the outside is not strictly proportional to either the average or the maximum temperature rise. Another possibility for explaining the high temperature rises observed with ethyl azide lies in the assumption that intermediate products, probably free radicals, are recombining on the surface of the wire and thereby giving out heat, and that this occurs more readily with ethyl azide than with azomethane. These various possibilities cannot be resolved until further experimental data are available. We hope that it will be possible to get such data, and in the meantime it does not seem worth while to present in detail the results so far at hand.

7. Summary

1. The pressure limit for the explosion of ethyl azide has been determined as a function of the temperature for the pure gas, and for mixtures with helium and carbon dioxide. Mixing with helium raises the critical pressure, while carbon dioxide has no effect. Decreasing the size of the reaction flask raises the critical pressure.

2. The Semenov theory of thermal explosions, by which the heat of reaction accumulating in a reacting gas leads under certain conditions to an explosion, has been applied to the data, and found to explain them in a reasonably satisfactory way.

3. The explosion has been compared with that of azomethane. In general, the phenomena are similar, but in certain details there are differences, which have been pointed out.

CAMBRIDGE, MASS.

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