pendent of any assumption regarding the 0.1 N calomel electrode. Values of the salting-out constant, Ks, and of b, have been estimated for solutions varying in molecular concentration from 0.02 to 4 M, and in the mole fraction as CH_3COONa from 0.1 to 0.9.

8. Interpolation tables and graphs are given to facilitate the preparation of buffer solutions of the same ionic strength and varying P_H, or of the same P_H and varying ionic strength.

9. These measurements upon acetate mixtures together with those already published upon phosphate mixtures render it possible to prepare buffer solutions of known ionic strength at any reaction between P_H 3.6 and 7.6.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE DECOMPOSITION OF AZO-ISOPROPANE. A HOMOGENEOUS UNIMOLECULAR REACTION

BY HERMAN C. RAMSPERGER[1]

RECEIVED NOVEMBER 29, 1927 PUBLISHED MARCH 7, 1928

The decomposition of azomethane was found to be first order at high pressures[2] but at lower pressures a reduction in the rate constant was found.[3] This result has been accounted for on one of the theories (Theory II)[4] of unimolecular gas reactions developed by Rice and Ramsperger.[5] It was to be expected that other azo compounds would also decompose in unimolecular manner and that the higher, more complex azo compounds would maintain the same rate constant to lower pressures than does azomethane. In this research the rate of reaction of azo-*iso*propane has been determined at initial pressures from 4.60 cm. to 0.025 cm. and at temperatures from 250 to 290°.

Reaction Products

Azomethane reacted principally according to the equation $CH_3NNCH_3 = N_2 + C_2H_6$. A small amount of side reaction could be attributed to either of the following reactions.

$$2CH_3NNCH_3 = 2N_2 + C_2H_4 + 2CH_4$$
$$CH_3NNCH_3 = N_2 + C_2H_4 + H_2$$

The final pressure was 2.04 times the initial pressure instead of exactly 2 times, due to one or both of these side reactions. The complete decomposition of azo-*iso*propane at constant temperature and constant

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[1] National Research Fellow in Chemistry.

[2] Ramsperger, THIS JOURNAL, **49**, 912 (1927).

[3] Ramsperger, *ibid.*, **49**, 1495 (1927).

[4] Rice and Ramsperger, *ibid.*, **49**, 1617 (1927).

[5] Rice and Ramsperger, *ibid.*, **50**, 617 (1928).

volume gave an average final pressure of 2.15 times the initial pressure. The main reaction and side reactions analogous to azomethane are

$$C_3H_7NNC_3H_7 = N_2 + C_6H_{14} \qquad (1)$$
$$C_3H_7NNC_3H_7 = N_2 + C_3H_6 + C_3H_8 \qquad (2)$$
$$C_3H_7NNC_3H_7 = N_2 + C_6H_{12} + H_2 \qquad (3)$$

One can distinguish between Side Reactions (2) and (3) by freezing out all of the hydrocarbons with liquid air. From the final pressure value given above and assuming Equation (2), 53.5% of the gas should be condensable, and assuming equation (3) 46.5% should be condensable. Two results of 53.0 and 53.8% show that the final pressure can be accounted for if 85% reacts according to Equation (1) and 15% according to Equation (2).

The Preparation of Azo-isopropane

Azo-*iso*propane was prepared by the method of Lochte, Noyes and Bailey.[6] Symmetrical di-*iso*propylhydrazine hydrochloride was prepared by the method of Lochte, Bailey and Noyes.[7] It was recrystallized twice from absolute alcohol. An alkaline solution of the compound was treated with an excess of copper acetate and the azo-*iso*propane distilled. It was dried with calcium chloride, redistilled and finally was very slowly distilled at 0° through soda lime and calcium chloride in a vacuum line. It was freed from air in the same manner as was azomethane.[2] The supply of gas for some of the decomposition experiments was contained in a 700-cc. bulb which was painted black to prevent possible decomposition by light. For some of the lower pressure experiments a 250-cc. bulb was used with a capillary tube between the bulb and the reaction cell. For the lowest pressure experiments the desired amount of gas was allowed to flow through the capillary into the tubing leading to the cell but was prevented from flowing into the cell by a mercury U-trap. By lowering the mercury in this trap, the gas could be let into the cell and a pressure measurement usually made within ten seconds. The decomposition during this period would be negligible at the lower temperatures but a small correction of at most several per cent. was made at high temperatures, the amount of the correction being usually determined by the final pressure obtained. One sample of azo-*iso*propane was used for Expts. 1 to 18, inclusive. The bulb was filled from the same liquid four times. The first filling was for Expt. 1, the second for Expts. 2 and 3, the third for Expts. 4 to 8, inclusive, and the fourth from 9 to 18, inclusive. Examination of the results shows that the constants did not vary with the fraction of the sample used. However, a new sample of liquid made from a different sample of di-*iso*propylhydrazine hydrochloride gave somewhat lower and irreproducible constants at the same pressure range as Expts. 13 to 18. Another

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[6] Lochte, Noyes and Bailey, This Journal, **44**, 2556 (1922).

[7] Lochte, Bailey and Noyes, *ibid.*, **43**, 2597 (1921).

sample was made more carefully and gave the results of Expts. 19 to 26. These experiments were made to test the effect of increased surface and were sufficiently reproducible for this purpose, but are all somewhat lower and were not used to determine the heat of activation.

Pressure Measurements

The reaction cell and thermostat were the same that were used in the experiments with azomethane.[2] The Pyrex reaction cell is ring-sealed into an outer chamber in which mercury is boiled under a known pressure. The rate of the reaction was determined by pressure measurements with a McLeod gage in much the same way as with azomethane.[3] In this case, however, the McLeod gage and mercury trap were surrounded by an air-bath at a temperature of 80° for Expts. 1 to 18 and 50° for Expts. 19 to 26. This was necessary to prevent condensation of the gas in the capillary of the McLeod gage. The calculation of the partial pressure of azo-*iso*propane in the reaction cell at the beginning and end of each time interval was the same as in the previous paper.[3] This calculation was made as follows.

Let P be the pressure read on the gage. Let the pressures in the reaction cell be designated as follows: P', the pressure before the reading was made; P'', the pressure after the reading was made; P'_A, the partial pressure of azo-*iso*propane before each reading; P''_A, the partial pressure of azo-*iso*propane after each reading. Let V be the volume of the reaction chamber, V_1 the volume of the trap and V_2 the total volume of the McLeod gage. Let T_1 be the temperature of the trap and gage and T_2 the temperature of the reaction cell. Let N_1 be the number of moles of gas in the trap and N_2 the number of moles in the reaction cell. We can calculate P'' in terms of P and the temperature and volume constants as follows. $PV_1 = N_1RT_1$, $PV = N_2RT_2$, $P''V = (N_1 + N_2)RT_2$. Eliminating N_1 and N_2 we find $P'' = P(V_1T_2/VT_1 + 1)$. P' may be calculated as follows. Let N_8 be the number of moles passing into the gage only, when the mercury is lowered for a reading. Let ΔP be the increase in pressure read on the gage in two successive readings. Then $\Delta PV_2 = N_8RT_1$ and $P_1'V = (N_1 + N_2 + N_3)RT_2$; $P' = P'' + \Delta PV_2T_2/VT_1$. Now the increase in pressure in the reaction cell, after one reading was made at time t and before the next reading at time t', is $P'_{t'} - P''_t$. If this increase be divided by 1.15, we get the change in azo-*iso*propane pressure. Therefore we have the relation $P'_{At'} = P''_{At} - (P'_{t'} - P''_t)/1.15$; also, $P''_{At} = P'_{At}\ P''_t/P'_t$. The first order rate constants were then calculated from the relation $K = \log_{10} P''_{At}/P'_{At'} \times 2.303/(t' - t)$, where t and t' are given in seconds.

Experimental Results

A summary of all of the experiments except Expts. 10 and 15, in which some gross error was made, is given in Table I and the complete data of three typical experiments are given in Table II.

The $\log_{10}$ of the average constant at each temperature is plotted against the reciprocal of the absolute temperature in Fig. 1. The slope of the straight line multiplied by 2.303 R is the "heat of activation," Q, as given by the Arrhenius expression for the temperature coefficient of reaction rate which is $(d \ln K/d)1/T = Q/R$. The intercepts of the straight line

Table I

Summary of All Experiments

Expt. no.	Temp., °C.	Init. pressure, cm.	Av. $K \times 10^3$	Expt. no.	Temp., °C.	Init. pressure, cm.	Av. $K \times 10^3$
12	250	1.771	0.451	7	280	3.080	3.88
13	250	.388	.461	8	280	.770	3.96
18	250	.0785	.467	11	290	.3685	7.96
4	260	4.60	1.03	16	290	.0919	7.46
1	260	4.09	.98	24	270	.137	1.90
2	260	2.94	1.00	25	270	.113	1.86
3	260	1.75	.98	19	270	.106	1.84
17	260	.0926	1.02	21	270	.097	1.85
5	270	3.515	1.99	23	270	.0850	1.84
9	270	1.917	2.01	22	270	.0550	1.95
6	270	.649	2.14	26	270	.0283	1.80
14	270	.0857	2.04	20	270	.0257	1.81

Table II

Complete Data of Three Experiments

Expt. 5. $V_1T_2/VT_1 = 2.8 \times 543/2.10 \times 353 = 0.020$; $V_2T_2/VT_1 = 11.14 \times 543/2.10 \times 353 = 0.082$; decomposition in filling cell = 0.035 cm.

t, min.	0	3	6	9	12	17	35
P, cm.	3.480	4.630	5.390	5.885	6.220	6.555	7.000
P''	3.550	4.725	5.500	6.005	6.345	6.690	7.140
P'	...	4.819	5.562	6.056	6.372	6.717	7.148
P'_A	...	2.377	1.602	1.099	.772	.446	.021
P''_A	3.480	2.330	1.582	1.091	.769	.444	.021
$K(\times 10^3)$	...	2.12	2.08	2.02	1.92	1.82	...

Expt. 25. $V_1T_2/VT_1 = 2.8 \times 543/168 \times 323 = 0.028$; $V_2T_2/VT_1 = 8.90 \times 543/168 \times 323 = 0.089$

t, min.	0	2	4	.6	9	16
P, cm.	0.110	0.132	0.152	0.165	0.183	0.208
P''	.113	.136	.156	.170	.188	.214
P'	...	.138	.158	.171	.190	.216
P'_A	...	.091	.071	.057	.040	.016
P''_A	.113	.090	.070	.057	.040	.016
$K(\times 10^3)$	...	1.80	1.98	1.71	1.97	...

Expt. 17. $V_1T_2/VT_1 = 2.8 \times 533/210 \times 353 = 0.020$; $V_2T_2/VT_1 = 8.90 \times 533/210 \times 353 = 0.064$

t, min.	0	4	8	12	19
P, cm.	0.0908	0.1102	0.1260	0.1396	0.1580
P''	.0926	.1127	.1285	.1424	.1612
P'	...	.1140	.1296	.1433	.1624
P'_A	...	.0740	.0585	.0452	.0275
P''_A	.0926	.0732	.0581	.0449	.0273
$K(\times 10^3)$	...	.93	.93	1.05	1.17

are for $1/T = 0.00177$ $\log_{10} K = -2.06$ and for $1/T = 0.00192$ $\log_{10} K = -3.40$. Q is found to be 40,900 cal. per mole. The rate constant $K = 5.6 \times 10^{13} \times e^{-\frac{40900}{RT}}$.

Expts. 24, 25 and 26 were made with enough small Pyrex tubing in the cell to make the surface six times as great. They are to be compared to five other experiments at that temperature and from the same sample, namely, 19, 20, 21, 22 and 23. The average rate constant of these five is 1.86×10^{-3} and of the three with tubing 1.85×10^{-3}. It is apparent that the reaction rate is not influenced by increase of wall surface and that the reaction is therefore homogeneous. It is also evident from the two experiments at the lowest pressures, that is, Expts. 20 and 26, that within experimental error there is no change in the rate constant at this low pressure.

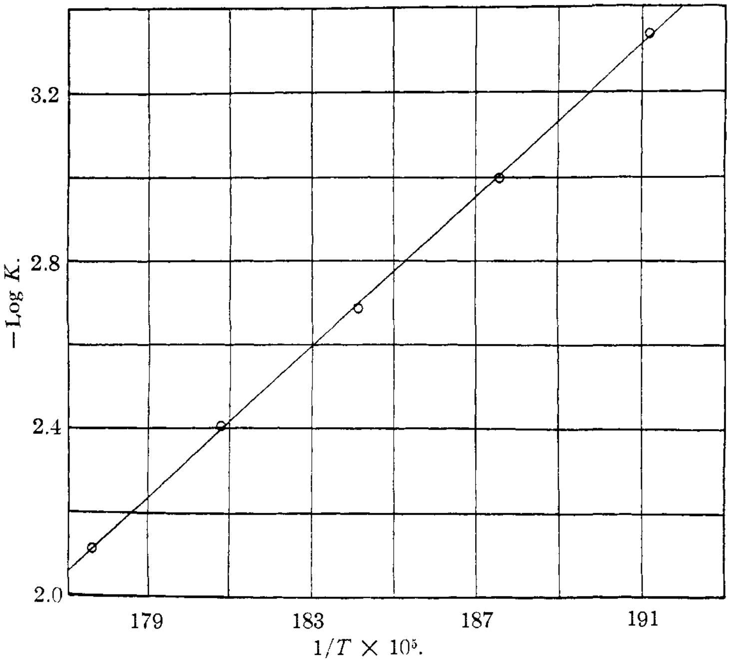

Fig. 1.

Theoretical

The results indicate that the more complex azo-*iso*propane maintains a constant value of the rate constant to low pressures where azomethane deviates greatly from the high pressure rate. In the case of azomethane the rate constant was appreciably below the high pressure rate constant at 4 cm. initial pressure and became steadily lower as the initial pressure was decreased until at 0.025 cm. the rate had dropped to 22% of the high pressure value when the temperature was 290° and to 10% for 330°.[3] It has been found that Theory II of Rice and Ramsperger[4] explains all of the rate constants of azomethane over the 3000-fold pressure range if 25 internal degrees of freedom are used.[5] Theory I by the same authors does not fit the data. Twenty-five degrees of freedom is a reasonable value for this molecule. The specific heat (C_v) of the gas would then be expected to be about 28 cal. per mole at a temperature of 300°, since each degree of freedom is equivalent to $^1/_2R$ cal. per mole and the three translational degrees of freedom are to be added. The specific heat of azomethane is not known but acetone might be expected to have a similar specific heat. Its specific heat (C_v) at 26 to 110° is 18.1 cal. and at 129 to 233° it is 21.9 cal. per mole, so that the twenty-five degrees of freedom required to fit the data is a reasonable value. If we apply either Theory I or Theory II to azo-*iso*propane, we find that 45 to 50 degrees of freedom will be required if the same rate constant is to be maintained to 0.0257 cm. initial pressure. The very large specific heat which is required is not impossible for such a large molecule. Azomethane has 10 atoms and 10 chemical bonds while azo-*iso*propane has 22 atoms and 22 chemical bonds, so that we might expect a specific heat about twice as great for azo-*iso*propane. Theory I is an extension of the theory of Hinshelwood and Lindemann[8] so that their theory likewise requires this large number of degrees of freedom. The theory of Fowler and Rideal[9] was used by Bernard Lewis[10] to explain the decomposition of azomethane before the data on azomethane at low pressures were published. This theory has not been developed so far as to show the manner in which the rate will change at low pressures. It requires fewer degrees of freedom but has the disadvantages pointed out by Tolman, Yost and Dickinson.[11]

Other possible explanations of the rate of unimolecular reactions are the chain mechanism and the radiation hypothesis. A reaction chain mechanism has been shown to be impossible in the case of most unimolecular reactions[12] and it was shown by the author[13] that in the photochemical decomposition of azomethane with a light photon of much higher energy than the heat of activation, only two molecules were decomposed per photon absorbed. The radiation theory of chemical reaction has been definitely disproved in at least one instance by Lewis and Mayer.[14]

The theories which are still capable of explaining all of the first order gas phase reactions are all collision theories which in most instances depend upon rather large internal energies. It is noteworthy that these theories differ in the assumptions concerning energy transfer between molecules at collision and energy transfer within the molecule. Three cases may be mentioned.

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[8] Hinshelwood and Lindemann, *Proc. Roy. Soc.* (*London*), **113A**, 230 (1926).

[9] Fowler and Rideal, *ibid.*, **113A**, 570 (1927).

[10] Lewis, *Proc. Nat. Acad. Sci.*, **13**, 546 (1927).

[11] Tolman, Yost and Dickinson, *ibid.*, **13**, 188 (1927); Lewis, *Science*, **66**, 331 (1927), has corrected an error in this paper.

[12] Lewis and Smith, THIS JOURNAL, **47**, 1508 (1925); Tolman, *ibid.*, **47**, 1524 (1925).

[13] Ramsperger, *ibid.*, **50**, 123 (1928).

[14] Lewis and Mayer, *Proc. Nat. Acad. Sci.*, **13**, 623 (1927).

First, the theories of Hinshelwood and Lindemann,[8] and Theory I of Rice and Ramsperger, in which the *total energy* of the molecule should equal or exceed a minimum energy in order that the molecule be activated. Some of them react, but the chance of reaction is independent of the amount of energy in excess of this minimum. It is assumed that the rate of activation is equal to what the rate of deactivation would be under equilibrium conditions. The rate of deactivation is calculated on the assumption that *every collision of an activated molecule results in deactivation and the ordinary kinetic theory radius is used in this calculation.*

Second, the theory of Fowler and Rideal,[9] which requires that *if the sum of the energies of two colliding molecules is equal to or exceeds a certain minimum of energy, all of this energy is transferred to one molecule which is then activated.* Lewis[11] shows that in the case of N_2O_5 this leads to *a deactivation radius of* 6.07×10^{-6} *cm.*

Third, Theory II of Rice and Ramsperger,[4] in which the rate of deactivation and of activation is calculated as in Theory I. *In addition it requires that a particular degree of freedom get a minimum of energy after which reaction occurs immediately. It must be possible for energy to be redistributed among the various degrees of freedom within the molecule between collisions.*[15]

It seems likely that the conditions of energy transfer differ widely in different molecules and that as a consequence there may be reactions which will fit each theory and some reactions that are intermediate in type and cannot be fitted exactly by any of the above theories. Two evidences of variation in energy transfer may be cited.

First, the experiments of Stuart,[16] which show that the quenching of the resonance fluorescence of mercury differs very widely for different gases, being greatest for H_2 and least for He. Second, the experiments of Hinshelwood show that of a number of inert gases only hydrogen can maintain the high pressure rate constant of a "quasi" unimolecular reaction at low pressures. It may be expected that the fewer quantum states of simpler molecules will introduce special restrictions of energy transfer which would be far less likely to occur in the complex molecules which decompose in unimolecular manner.

Summary

The thermal decomposition of azo-*iso*propane has been studied at temperatures from 250 to 290°, at initial pressures from 4.60 cm. to

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[15] A fourth type which is not quite comparable with the three cases listed above is the theory of J. J. Thomsen [*Phil. Mag.* [7] 3, 241 (1927)], in which energy may be transferred from the fields of neighboring molecules. The energy of a given molecule "waxes and wanes" and thus at some instant may get sufficient excess energy from the field to cause reaction.

[16] Stuart, *Z. Physik*, **32**, 262 (1925).

0.025 cm. and with increased wall surface. The reaction was found to be homogeneous and unimolecular at all pressures.

The heat of activation as given by the Arrhenius expression for the temperature coefficient of reaction rate is 40,900 cal. per mole. The rate constant is given by the expression $K = 5.6 \times 10^{13} \times e^{-\frac{40,900}{RT}}$

A discussion of these results in relation to various theories of reaction rate is given. Theory II of Rice and Ramsperger would require that the rate constant of the reaction become smaller at pressures below 0.025 cm. if the azo-*iso*propane molecule had 45 to 50 degrees of freedom. It is thought likely that the specific heat of azo-*iso*propane would be large enough to permit this number of degrees of freedom.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 162]

THE REDUCTION POTENTIAL OF SELENIUM AND THE FREE ENERGY OF AQUEOUS SELENOUS ACID

BY HERMAN F. SCHOTT, ERNEST H. SWIFT AND DON M. YOST

RECEIVED DECEMBER 5, 1927 PUBLISHED MARCH 7, 1928

Introduction

The fact that selenous acid, H_2SeO_3, is reduced to elementary selenium by iodides in acid solutions is well known and is made use of in analytical methods for the determination of selenium.[1] The reduction, however, is quantitative only in moderately strong acid solutions. It was found, as a result of a number of preliminary experiments, that in more dilute acid solutions the substances taking part in the reaction are present in measurable amounts when equilibrium is attained.

In this paper are described equilibrium measurements at 25° for the following reaction, together with the thermodynamic quantities calculated from them, $Se(s) + 2I_2(s) + 3H_2O(l) = H_2SeO_3(aq) + 4H^+ + 4I^-$.

We wish to express here our appreciation of the many useful suggestions made by Professor A. A. Noyes. The investigation was aided on the financial side by funds granted to him by the Carnegie Institution of Washington.

Outline of the Investigation

The reaction mixtures were prepared by mixing standard solutions of selenous acid, potassium iodide, perchloric acid and water in 250cc. volumetric flasks and transferring the contents to glass-stoppered bottles

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[1] Muthman and Schäfer, *Ber.*, **26,** 1008 (1893); Gooch and Reynolds, *Z. anorg. Chem.*, **10,** 248 (1895).