constants based on the electromotive force measurements of pure acid are just as accurate as those based on the electromotive force measurements of acid plus sucrose solutions. The calculated velocity constants agree very well with those determined by experiment above 3 molal acid, for more dilute concentrations they are too high. This same discrepancy was noted in the previous paper, but it was hoped that when the activities of the sugar solutions were used for the theoretical calculations the discrepancy would disappear.

TABLE IV

m	*K* obs.	*K* calcd.	*K* calcd.
0.929	0.00215	0.00298	0.00302
1.908	.0066	.00775	.00784
2.904	.0147	.0156	.0160
3.666	.0251	.0252	.0255
4.025	.0316	.0312	.0316
5.349	.0667	.0660	.0667
6.095	.1030	.0991	.0992
7.730	.2260	.2400	.2380
8.468	.3540	.3530	.3510
9.846	.6880	.6880	.6930

Summary

1. The electromotive force measurements of hydrochloric acid and hydrochloric acid plus sucrose for 1 to 4 molal concentration have been measured at 20° and the activities calculated.

2. The velocity constants for (0.292 molal) sucrose hydrolysis with hydrochloric acid, varying in concentration from 1 to 9 molal, were determined.

3. A definite relationship between activities and velocity constants was noted using the electromotive force measurements of either the pure hydrochloric acid solutions or the hydrochloric acid containing sucrose, for calculating the activities.

HARTFORD, CONN. RECEIVED AUGUST 21, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Thermal Decomposition of Propylamine

BY DARRELL V. SICKMAN AND O. K. RICE

In the course of a study of a number of unimolecular reactions whose rate constants begin to decrease at pressures higher than would be expected from the size of the molecule involved, the decomposition of *n*-propylamine was carried to fairly low pressures in an attempt to discover whether the effect predicted by one of us[1] actually occurred. This reaction has been studied at moderate pressures by H. A. Taylor and Achilles,[2] who reported that it was homogeneous and apparently unimolecular, the rate falling off at pressures below 200 mm. Their results indicated extensive secondary reactions such as are met with in nearly all organic reactions that proceed at high temperatures. The effect of the inert gases hydrogen, helium and nitrogen was to decrease the rate markedly.

Experimental Method

The apparatus used was practically that described previously.[3] As stopcock grease is rapidly liquefied by propylamine vapor, mercury traps were used instead of stopcocks. The reaction vessel was a liter Pyrex flask placed in a fused salt thermostat whose temperature was regulated to ±0.2°. The reaction was followed manometrically, the lower pressures being read on a small multiple range McLeod gage. The results do not seem to warrant the small correction of 4–7% to the measured rates to correct for the external volume, but a correction for the material appearing slowly, apparently from the glass,[4] has been made for the runs at the lower pressures.

The propylamine used was purchased from the Eastman Kodak Co., and was purified by drying with fused potassium hydroxide and fractionating.

Results and Discussion

In view of the complexities of the reaction the rate constants calculated during the course of a run, which fall rapidly except in a narrow pressure range, are not useful. The rate constant reported has been calculated by graphical determination of the initial slope of the time–pressure curve of each run. The rate constant is then the ratio of this initial slope to the extrapolated initial pressure.[5] In order to minimize the rather large error possible in the determination of the initial slope, two separate calculations were made, and

---

(1) O. K. Rice, *Z. physik. Chem.*, **7B**, 226 (1930).

(2) Taylor and Achilles, *J. Phys. Chem.*, **35**, 2658 (1931).

(3) O. K. Rice and D. V. Sickman, THIS JOURNAL, **56**, 1444 (1934), Apparatus I.

(4) Reference 3, page 1447.

(5) The exact expression for the rate constant is, of course, $dp/dt/(n - 1)p$, where n is the number of molecules of product. The adopted expression assumes $n = 2$.

the results reported are the averages of these two series. The least square method used for ethyl ether[3] is preferable, but the method used is amply accurate to indicate the nature of this reaction.

The results of our experiments are summarized in Table I, and plotted in the figure. The data of two typical runs are given in Table II. In a few cases, namely, runs 20, 21, 23, 26 and 30, an induction period appears which is apparently outside the experimental error, but the conditions for its appearance were not defined. A typical example of a run with the induction period is given in Table III. The "initial slope" chosen in these cases was that after the induction period was apparently over.

TABLE I

Run	Initial press., mm.	$k \times 10^5$ sec.$^{-1}$
	500°	
14	0.286	13
13	1.39	8.5
12	1.40	15.5
39	4.68	16.0
6	7.50	17.8
5	11.8	19.1
4	34.7	34.8
	520°	
40	0.950	27.7
41	1.40	34.3
42	2.65	35.0
30	4.76	42.3
34	8.30	49.2
29	9.60	48.7
33	35.8	79.6
31	37.1	79.9
32	108	96.7
11	0.395	22.8
10	.800	27.2
7	16.1	56.8
8	32.4	72.3
9	174	100
	540°	
35	3.14	88.7
36	10.55	118
37	36.8	172
38	37.6	180
	520° 7 × surface	
25	0.125	16.0
23	.353	15.3
22	.706	16.3
21	2.53	17.2
18	3.06	17.5
20	3.16	16.9
19	4.35	16.6
17	5.80	16.9
24	10.08	22.1
43	19.1	32.9
15	34.7	68.8
16	209	126
	540° 7 × surface	
26	0.10	41
27	2.08	36.8
28	23.6	94.5

TABLE II

Run 38, 540°		Run 42, 520°	
Time, minutes	Press., mm.	Time, minutes	Press., mm.
1	41.7	2	2.766
3	49.2	5	2.942
5	55.2	8	3.107
7	60.1	12	3.357
10	66.0	16	3.558
12	69.2	20	3.781
15	72.9	25	4.038
81	90.4	33	4.414

TABLE III

Run 30, 520°

Time, minutes	Press., mm.	Time, minutes	Press., mm.
2	4.85	19	6.75
4	4.98	22	7.11
6	5.17	26	7.54
8	5.41	30	7.96
10	5.65	35	8.40
12	5.92	40	8.77
14	6.13	46	9.14
16	6.39	52	9.50

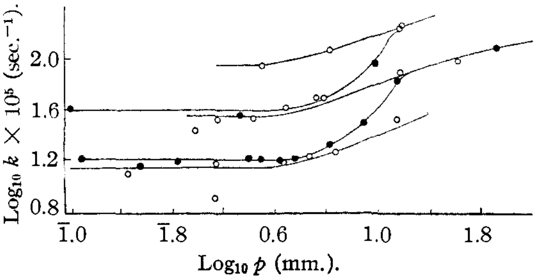

Fig. 1.—Variation of rate constant with pressure and surface: ○, empty vessel at 540, 520 and 500°; ●, vessel packed with 10 mm. tubing at 540 and 520°.

Runs 7–11 were made in a flask which had been washed in chromic acid cleaning solution. They are not plotted in the figure.

Regarding the results obtained, it is at once apparent that, whatever it may be, the reaction is not a straightforward homogeneous unimolecular decomposition. Increasing the surface about seven-fold by filling the vessel with short pieces of 10-mm. tubing with fire-polished ends is without effect at pressures above 200 mm., but decreases the rate by about 40% below about 4 mm. Even etching the surface decreases the rate (Runs 7–11). The general shape of the log p-log k curve is that which we hoped to find, but the effect of increasing the surface shows this theory[1] to be inapplicable.

No satisfactory explanation of the course of this reaction can be offered. If the reaction were a chain, all chains being broken on the walls at low pressures and in the gas phase at high pressures, we should get a log p-log k curve with at least qualitatively the shape found; but this is not adequate to account for the effect of foreign gases observed by Taylor and Achilles. The chain breaking mechanism may require three-body collisions, the third body being the wall or a gas molecule; or there may be a polymerization reaction of the products requiring a third body, but the absence of tar production in the reaction indicates that this is unlikely. It is possible that the reaction which we observed was a different one than that of Taylor and Achilles, as our rates are about half theirs. This corresponds to a difference of nearly 20° in the absolute temperatures, which seems a little large to be ascribed to experimental error. It should be noted, however, that the kinetics of the propylamine decomposition which we find correspond in detail to those for ethylamine found by Schumacher and Wiig,[6] whose rates are also considerably slower than those of Taylor.[7] We also find a somewhat larger temperature coefficient than do Taylor and Achilles; we find about 51 Cal. compared to their 44 Cal., but as it seems to have but little significance the details of the calculation are not given here.

Summary

The thermal decomposition of *n*-propylamine has been extended to low pressures. Below 4 mm. the reaction is first order, but is strongly inhibited by increased surface; this effect diminishes and finally disappears at higher pressures. The reaction is probably a chain.

CAMBRIDGE, MASS. RECEIVED AUGUST 25, 1934

(6) Schumacher and Wiig, *Z. physik. Chem.*, **162A**, 419 (1932).

(7) H. A. Taylor, *J. Phys. Chem.*, **34**, 2761 (1930).

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Vapor Pressures and Activity Coefficients of Aqueous Solutions of Calcium and Aluminum Nitrates at 25°[1]

BY J. N. PEARCE AND L. E. BLACKMAN

In recent papers[2] were reported the vapor pressures and the activity coefficients of aqueous solutions of several strong binary electrolytes. The present paper deals with the results of a similar study of aqueous solutions of calcium and aluminum nitrates.

The apparatus employed is exactly the same as that used in the previous work, except that the number of electrolytic cells has been increased to forty. In this way the volume of electrolytic gas generated per equivalent of silver has been doubled and the errors of measurement have been reduced considerably.

The "analyzed" salts were further purified by repeated crystallization. Nearly saturated mother solutions of each salt were prepared and the weight composition of each was determined accurately by approved methods. Definite weights of these solutions were diluted with conductivity water to give the desired weight molal concentration. The density of each solution was determined accurately by means of a 100-cc. pycnometer recently devised by Pearce. Duplicate weights of the solutions used in the density measurements check easily to one part in one million. All weighings were made with certified brass weights and are corrected for air buoyancy (N. T. P.).

The essential data for the two nitrates are collected in Tables I and II. Each value of p indicated is the mean of three to six independent vapor pressure measurements. The maximum deviation from the mean for any solution did not exceed 0.003 mm. The remaining familiar symbols require no explanation.

TABLE I

VAPOR PRESSURE, ACTIVITY AND FREE ENERGY DATA OF AQUEOUS SOLUTIONS OF CALCIUM NITRATE AT 25°

m	p, mm.	a_1	$h/m^{1/2}$	$\gamma_{\pm}$	$-\Delta\bar{F}_1$, cal.	$-\Delta F_2^{0.1}$, cal.
0.0	23.752	1.0000	1.365	1.000	....	...
.1	23.659	0.9961	0.868	0.661	2.32	0000
.2	23.566	.9922	.587	.551	4.72	908
.4	23.373	.9841	.405	.452	9.53	1788
.6	23.160	.9751	.286	.396	14.96	2275
.8	22.915	.9647	.190	.356	21.26	2598
1.0	22.638	.9531	.111	.325	28.48	2831
1.5	21.868	.9207	− .016	.351	48.98	3691
2.0	21.002	.8843	− .097	.411	72.88	4479
2.5	20.042	.8438	− .162	.558	100.7	5425
3.0	19.107	.8044	− .198	.684	129.0	6110
3.5	18.118	.7628	− .231	.821	160.5	6708
4.0	17.098	.7198	− .260	1.036	194.9	7359
5.0	15.008	.6319	− .312	1.516	272.1	8433
6.0	13.062	.5499	− .345	2.035	354.5	9280
7.0	11.260	.4741	− .368	2.612	442.4	9999
8.0	9.603	.4043	− .386	3.211	536.8	10603
8.3601[a]	9.041	.3806	− .394	3.486	572.5	10827

[a] Saturated. $a_2 = 27(\gamma m)^4$.

The activity of the water, a_1, in the various solutions may be calculated directly from the

(1) A brief abstract of a dissertation presented to the Graduate College of the State University of Iowa by Leslie Everett Blackman in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

(2) Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932); **55**, 3075 (1933).