literature[6] concerning the chemical properties of pure apocodeine.

The herein described method is an improvement of the Knorr reaction, and a confirmation of Knorr's properties of apocodeine with ethanol of crystallization. The pure anhydrous base and hydrochloride have not been described previously.

Apocodeine.—Twenty grams of anhydrous codeine and 60 g. of anhydrous oxalic acid,[7] were heated for one and one-half hours at 150–155° bath temperature with very slow stirring. The melt was cooled and diluted with 250 ml. of water. After complete solution, it was further diluted to 600 ml. in a separatory funnel, shaken with 300 ml. of ether, and the bases precipitated with addition of concentrated ammonia solution. Too slow operation caused troublesome crystallization of ammonium oxalate. The ether layer was separated, filtered and distilled *in vacuo*. A residue of 5.8 g. remained, which was dissolved in 15 ml. of absolute ethanol. Nearly pure apocodeine with a molecule of ethanol crystallized on standing at 10°; yield 2.7–2.8 g. (12.8%). One crystallization gave pure white products of m. p. 104.5–106.5° with gas evolution $[\alpha]^{23}_{D}$ −90.0, *C*, 0.533, abs. ethanol, *l* = 1. Further crystallization did not change the melting point or optical rotation.

Anal. Calcd. for $C_{18}H_{19}O_2N\cdot C_2H_5OH$: C, 73.35; H, 7.70; C_2H_5OH, 14.06. Found: C, 72.99, 73.01; H, 7.57, 7.76; C_2H_5OH, 13.76.

The base was best purified by recrystallization from absolute ethanol. The use of the hydriodide as Knorr suggested resulted in partial oxidation. The crystals showed no ready tendency to oxidize, unless they were finely pulverized. The ethanol was lost very slowly at 25° (2 mm.), but readily at 78° (2 mm.). The anhydrous base showed m. p. 122.5–124.5°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.82; H, 6.81. Found: C, 76.63, 76.80; H, 7.02, 7.06.

As Knorr described, there were ether and water insoluble bases present. It was found, however, that nearly all the apocodeine was extracted by the ether. In one experiment very little more was obtained by redissolving the insoluble bases with acid, reprecipitating, extracting etc. A third repetition of this process yielded no more apocodeine. Thus it was not necessary to bring all the precipitated bases into ether solution as Knorr described. In fact, the moderate insolubility of pseudocodeine[8] and the amorphous products in ether make the first extraction one of considerable purification.

Apocodeine Hydrochloride.—To a solution of the base in absolute ethanol was added the calculated amount of dry hydrogen chloride in absolute ethanol and, while hot, absolute ether was added until crystallization started. The yield of pure white salt was quantitative; m. p. softening started at 140°, dec. at 260–263°; $[\alpha]^{22}_{D}$ −41.3 to 43.3°; *c*, 0.508; H_2O, *l* = 1. Recrystallization from 95% ethanol and ether did not alter the physical constants. The salt was practically anhydrous.

Anal. Calcd. for $C_{18}H_{19}O_2N\cdot HCl$: C, 68.00; H, 6.35. Found: C, 68.26, 67.92; H, 6.35, 6.22.

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[6] For example, see Krayer, *Arch. exptl. Path. Pharm.*, **111**, 60 (1920). Schwartze, *Arch. intern. pharmacodynamie*, **41**, 461 (1931).

[7] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 415.

[8] Lutz and Small, THIS JOURNAL, **54**, 4723 (1932).

The Thermal Decomposition of Acetone

By JOHN R. HUFFMAN[1]

The present experiments were undertaken to discover whether the unimolecular rate constant for the thermal decomposition of acetone fell off at low pressures and in such a case to apply the theories of Rice and Ramsperger and of Kassel.[2] Recently Winkler and Hinshelwood[3] working at 875°K. and pressures down to 2.5 mm. reported that this decrease of rate constant started at 100 mm.

Acetone was decomposed in a 200-cc. silica bulb in a furnace automatically controlled to

TABLE I

Run	P_0, mm.	$k \times 10^4$	Run	P_0, mm.	$k \times 10^4$
59	128.6	10.86	46	56.2	9.70
65	127.2	11.39	63	55.9	9.85
64	124.3	11.17	42	53.5	9.41
69	120.4	10.72	22	47.8	9.38
71	115.5	11.42	37	45.9	8.80
58	112.6	11.33	35	41.6	8.68
73	107.0	10.96	24	34.9	9.05
72	101.2	10.32	75	35.2	8.50
57	100.2	10.69	76	35.1	8.66
61	100.2	11.31	36	27.8	8.12
66	99.0	11.27	32	27.8	7.98
70	98.6	11.35	45	25.6	8.18
60	86.7	10.78	31	22.9	7.65
68	83.4	10.42	23	21.5	8.07
74	80.4	10.60	52	21.85	8.36
50	78.8	10.93	34	18.54	7.43
40	78.3	10.75	29	17.86	7.68
51	78.2	10.48	27	17.08	7.43
55	74.3	10.79	44	16.60	7.48
62	79.1	10.32	43	16.53	7.37
56	76.3	10.13	25	15.53	6.83
49	72.5	10.53	33	12.80	6.86
39	72.9	10.60	30	9.71	5.92
41	66.0	9.79	28	7.51	5.51
48	62.1	10.08	26	7.49	5.40
38	60.7	9.54	54	5.65	5.06
47	57.7	9.90	53	4.68	4.50
67	58.5	9.88			

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[1] Sterling Research Fellow in Chemistry, Yale University, 1933–1934.

[2] For a detailed discussion and references see Kassel, "Kinetics of Homogeneous Gas Reactions," A. C. S. Monograph No. 57, Chemical Catalog Company, New York, 1932.

[3] Winkler and Hinshelwood, *Proc. Roy. Soc.* (London), **A149**, 340 (1935).

±0.2°. Pressures were read either on a mercury or a bromonaphthalene–mercury manometer. Experimental errors were smoothed out by a process of graphical differentiation and re-integration.[4] To correct for dead space (1.7%) the rate constants were calculated by the method suggested by Allen.[5] These constants fell off during a run due to the second step in the decomposition and consequently were extrapolated to zero time. The results, corrected slightly to 826°K., are presented in Table I.

A second series of runs was made to determine the temperature effect of the high pressure reaction. This is expressed by the equation

$$\ln k_\infty = 34.52 - 68120/RT$$

and is shown in Table II.

TABLE II

T., °K.	817	826	836	845.5	854
$k_\infty \times 10^4$	5.85	9.3	15.41	24.18	34.88

A plot of k *versus* P_0 ($k_\infty = 0.001125$ at 826°K.) establishes 100 mm. as the pressure where the reaction commences to fall off, checking the results of previous workers. A plot of $1/k$ versus $1/P_0$ indicates a break at 40 mm. pressure suggesting a second mode of activation.

Application of Hinshelwood's simple theory gives 22 active degrees of freedom. Using O. K. Rice's classical theory, 8 degrees of freedom and a molecular diameter of 28.3×10^{-8} cm. appear to be the best values to use. Kassel's quantum theory gives curves that fit the experimental results the best. The most reasonable values in this case appear to be 8 degrees of freedom, 22 quanta, and a diameter of 45×10^{-8} cm. This gives a frequency in the infra-red and a vibrational specific heat contribution of 12 cal./g. The results of Winkler and Hinshelwood at 875°K. are satisfied by 8 degrees of freedom, 22 quanta and 35×10^{-8} cm. Table III gives a comparison of the experimental and calculated results.

TABLE III

	826°K.		875°K.[a]	
P_0, mm.	k/k_∞ exptl.	k/k_∞ calcd.	k/k_∞ exptl.	k/k_∞ calcd.
200		0.916		0.855
100	1.000	.864	1.000	.780
50	0.865	.791	0.708	.685
20	.675	.664	.540	.540
10	.537	.555	.437	.427
5	.426	.439	.344	.320

[a] From the work of Winkler and Hinshelwood.

It was impossible to obtain a fit of theory to experiment throughout the whole pressure range. The calculated results fit within the experimental error from about 50 mm. pressure down. The rate constant falls off with decreasing pressure rather abruptly in comparison with other unimolecular reactions in such a manner as to indicate a free radical chain mechanism as proposed by F. O. Rice and Herzfeld.[6] This is further substantiated by the recent publication of A. O. Allen.[7]

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[4] Nybölle, *Nordisk Statistisk Tidskrift*, **8**, 103 (1929), Stockholm Aftonbladets Tr.

[5] Allen, THIS JOURNAL, **56**, 2053 (1934).

[6] F. O. Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

[7] Allen, *ibid.*, **58**, 1052 (1936).

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Semiquinones of Neutral Red and Safranines

BY LEONOR MICHAELIS

Many derivatives of phenazine have been shown to form semiquinones on partial reduction, all of green color in compounds containing only benzene and no naphthalene rings. The separation of the two steps of reduction is more distinct as the acidity of the solvent increases. The degree of acidity at which a distinct separation of the steps becomes easily recognizable varies from dye to dye. So far, no semiquinone has been observed in a number of those phenazine or phenazonium compounds containing amino groups as side chains. However, even in these compounds a semiquinone will be demonstrated by the following experiment, in which the conditions of reduction are slightly changed. One simply has to work in extremely acid solution. The experiment can be performed with neutral red, phenosafranine or the commercial "safranine."

Dissolve a small amount of the dye in concentrated hydrochloric acid. The color will be, according to the dye, blue to green. Dilute with water just enough to make it blue, with a shade of violet. Add some particles of solid chromous chloride and stir. The color will change first to an intense green, then to the almost colorless condition of the leuco dye. On reoxidizing, say by adding a crystal of potassium persulfate, the twofold change of color will be reversed. Zinc dust may also be used as reductant.

Since the color of the oxidized form of the dye in utmost acid solution (especially in concentrated sulfuric acid) itself is green, the acidity has to be lowered just to such an extent as to make it blue-