±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_∞ = 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

P_0, mm.	826°K.		875°K.[a]	
	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).

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONN.
RECEIVED MARCH 11, 1936

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-violet before adding the reductant. Otherwise there is no visible change on reducing the dye to the semiquinone state.

FROM THE LABORATORIES OF
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Polymolecular Films

BY WILLIAM D. HARKINS AND ROBERT J. MYERS

Surface films which spread over water are supposed to be monomolecular. However, Harkins and Morgan[1] were able to produce solid, partly crystalline films with a mean thickness much greater than this. Thus to a spreading substance whose organic molecules contain a polar group (stearic acid, etc.) they added a thickening or nonpolar substance (phenanthrene). In the present work polymolecular liquid films were produced by thickening the films with a liquid paraffin oil (nujol) of low volatility.

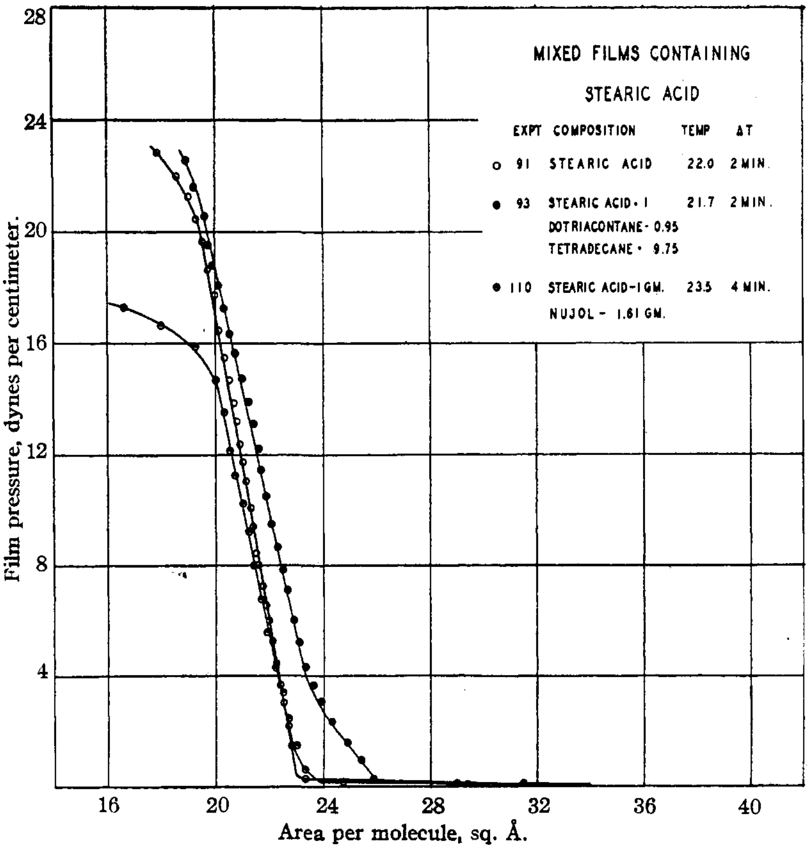

Fig. 1.—Poly- and mono-molecular films with stearic acid.

1. Condensed Films.—Films of pure stearic acid form condensed films on 0.01 N hydrochloric acid at room temperature except at pressures below about 0.2 dyne per cm. The addition of 1.61 g. of nujol to 1 g. of stearic acid in the film forming substances does not seem to increase the area of the condensed film (Fig. 1, expts. 91 and 110), but only weakens it at high pressures.

The areas given in the figures of this paper represent the area per molecule of the more polar constituent (stearic acid, etc.).

2. Expanded Films of Oleic Acid.—The effects are, however, markedly different in cases in which the acid when alone forms an "expanded" film, as in the case of oleic acid (Fig. 2). Here the mixed film contains 1.66 parts by weight of the paraffin oil to 1 part of oleic acid. The effect of the paraffin oil is very great, since it raises the surface pressure greatly at large areas, and decreases it very markedly at low areas. At 36.4 sq. Å. per molecule of oleic acid the pressures are the same for the pure acid and the mixture.

3. Expanded Films of Myristic Acid.—At 22.8° films of pure myristic acid exhibit a kink in the curve at an area of 25.45 sq. Å. and a pressure of 17.25 dynes per cm. The addition of 1.67 parts

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[1] Harkins and Morgan, *Proc. Nat. Acad. Sci.*, **11**, 631 (1925).