TABLE I

THIOURETHANS AND HYDROCHLORIDES

Thiourethan	Yield, %	M. p., °C.	Hydrochlorides: Yield, %	M. p., °C.	Formula	S Found	S Calcd.	Cl Found	Cl Calcd.
β-Diethylaminoethyl phenyl	62	Oil	49	121–2	$C_{13}H_{21}ON_2ClS$	11.10 10.96	11.10	12.17 12.13	12.28
β-Diethylaminoethyl *p*-dimethylaminophenyl	40	76	83	162–3d	$C_{15}H_{26}ON_3ClS$			10.86 10.90	10.69
γ-Diethylaminopropyl phenyl	41	76–77	66	98–100d	$C_{14}H_{23}ON_2ClS$			11.82 11.93	11.72
β-4-Morpholinoethyl phenyl	58	109	61	156–6.5	$C_{13}H_{19}O_2N_2ClS$	10.66 10.70	10.59	11.85 11.80	11.71
β-4-Morpholinoethyl *p*-dimethylaminophenyl	57	97	81	166	$C_{15}H_{24}O_2N_3ClS$			10.39 10.20	10.25

TABLE II

ANALGESIC, HYPNOTIC, ANESTHETIC AND TOXICITY TESTS

Phenylthiourethan hydrochloride = R Phenylthiourea hydrochloride = R₁	Mice, M. L. D. mg./g.	Intraperitoneally analgesic effect	Local anesthetic tests: Rabbit cornea—1% concn. at 1 min.	Rabbit cornea—1% concn. duration, min.	Rabbit cornea—1% concn. irritation	Frog sensory nerve[a] Anesthesia complete at min. 1%	0.5%	0.25%
β-Diethylaminoethyl-R	0.18	Slight?	Good	5	Slight	5	10	13
β-Diethylaminoethyl-*p*-dimethylamino-R	.10	None	Good[b]	14	Slight	8	15[c]	..
γ-Diethylaminopropyl-R	.15	Slight?	Good	8	Some	7	8	12
β-4-Morpholinoethyl-R	.35	None	Good	2	Some	7	10	..
β-4-Morpholinoethyl-*p*-dimethylamino-R	.20	Slight?	Some	3	Slight	8	11?	..
N-(β-4-Morpholinoethyl)-N′-R₁	.35	Slight?	None	..	....	..[d]	...	..
N-(β-4-Morpholinoethyl)-N′-*p*-dimethylamino-R₁	.40	Slight?	Slight?	..	....	..[d]	...	..
Procaine hydrochloride	.45			15		3	5.5	11
Cocaine hydrochloride	.10					..	2.5	9

[a] Averages of two determinations. [b] 0.5% concn. good at 2 min., duration 7 min. [c] Almost complete. [d] Not complete at 15 min.

They were also tested for possible analgesic or hypnotic action by gross observation of effects upon white mice following varied dosage given intraperitoneally. For analgesic tests the pain stimulus used was pinching of the tail, ears, and feet before and after administration of a dose of the compound. The toxicity tests were done on white mice injected intraperitoneally. The data are collected in Table II.

The pharmacological data may be summarized with the statements that the thiourethans showed pronounced local anesthetic activity, but were all considerably weaker than procaine hydrochloride, with appreciably greater toxicity. None of the compounds had any definite effects as analgesics or hypnotics.

Summary

1. Five new dialkylaminoalkyl arylthiourethans and two new dialkylaminoalkyl aryl thioureas have been prepared.

2. The thiourethans show fairly strong local anesthetic effects but no hypnotic or analgesic effects.

3. The thioureas are without anesthetic or hypnotic effects to any measurable degree.

ST. LOUIS, MISSOURI

RECEIVED AUGUST 4, 1941

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Changes in the Pressure of Monomolecular Films of Stearic Acid Due to Added Drops of Benzene

BY E. ROGER WASHBURN, LAURENCE F. TRANSUE[1] AND THEOS J. THOMPSON

It has been indicated[2] that it is possible to obtain a measurement of the pressure against which a liquid, such as benzene, will spread on a water surface by measuring the minimum pressure which will prevent the spreading. When benzene is dropped on a film of stearic acid which is under a lower pressure than the spreading pressure, each drop penetrates the film, spreads on the water and increases the film pressure. The increase in film pressure will be greater the larger the amount of benzene added, until the increased pressure equals the spreading pressure of the benzene. Addition of larger amounts of benzene will not cause the pressure to increase above this spreading pressure. Drops of benzene which are below a certain volume evaporate before the pressure has increased

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[1] Samuel Avery Research Fellow, 1940–1941.

[2] E. R. Washburn and Chris P. Keim, THIS JOURNAL, **62**, 1747, 2318 (1940).

to the spreading pressure. When the benzene is dropped on a film which is under a film pressure several dynes per centimeter greater than the spreading pressure, an immediate decrease in film pressure is noted.

These phenomena are clearly shown in Fig. 1. Curve A is the ordinary film pressure–area curve for a monomolecular film of stearic acid on water. An observation on any one drop of benzene is represented by two points, one on curve A and another (directly above or below the first) on curve B. The point on curve A represents the film pressure existing just before the drop of benzene was allowed to fall on the film. The point on curve B represents the maximum (or minimum) film pressure attained during the time that the benzene drop lay on the film. Curve B crosses curve A at a pressure which is slightly above the spreading pressure of benzene. The drops used in obtaining these curves were too small to permit the pressure to increase to the spreading pressure. Consequently there is no plateau in the portion of B which lies to the right of A.

This investigation is concerned with the time required for small, uniform drops of benzene to evaporate under different states of compression and with the changes in film pressure which occur during the life of a drop.

Materials and Apparatus

The stearic acid, benzene and water were essentially of the same quality as described in the previous reports.[2] The benzene froze at 5.44° and had a specific gravity d^{25}_4 0.8734. Care was taken to use only freshly redistilled water or that which had been stored for a short time in a bottle that had been used for years for the storage of conductivity water.

The chief difference in apparatus from that previously described was that the tray was constructed of bronze instead of aluminum. The tray and aluminum barriers were covered with many coats of Bakelite lacquer as described by McBain and Perry.[3] The same type of micro volume pipet was used for measurement of film material. The pipet used for the addition of drops of benzene to the film had a fine tip which delivered uniform drops of 0.0063 cc. volume. The pipet was mounted so that the tip was a constant distance above the film-covered water.

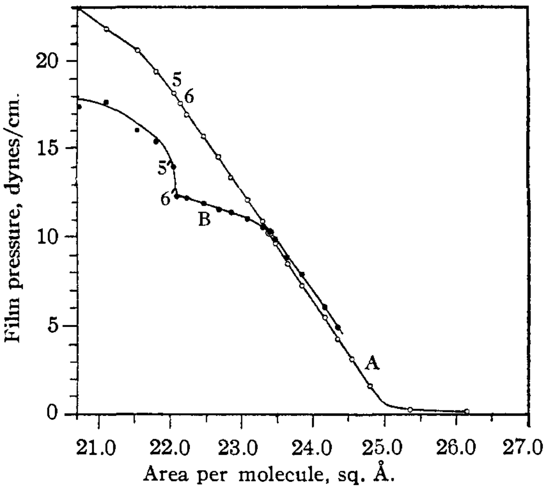

Fig. 1.

Experimental

A film of stearic acid on water was slowly compressed as in the usual determination of pressure–area curves. At intervals the compression was stopped, the film pressure and area were recorded, and a drop of benzene was allowed to fall on the film. During the life of the benzene drop, several simultaneous readings of film pressure and time were recorded. A stop watch was used for timing.

Results and Discussion

The results of typical experiments are plotted in Figs. 1, 2, and 3; Fig. 1 has been partially discussed in the introduction and another reference will be made to it. Each of the twelve curves in Fig. 2 represents a drop of benzene which was dropped on a stearic acid film under the initial film pressure indicated on the vertical axis for time equal to zero. The last point on each of the curves indicates the life of the drop in seconds and the film pressure observed as the drop disappeared. Intermediate pressures and corresponding times are shown.

The five drops at the lower pressures apparently penetrated the film and spread upon the water as thin layers. Evaporation of benzene prevented an increase to the spreading pressure (about 10 dynes per cm.). At the maximum of each curve the increase in pressure due to spreading was just balanced by loss of benzene due to evaporation. The pressure then decreased until the last of the benzene evaporated. The final pressures were essentially the same as the initial pressures. The sixth curve from the bottom shows a slight increase in pressure when the drop was first added,

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[3] McBain and Perry, *Ind. Eng. Chem.*, **31**, 35 (1939).

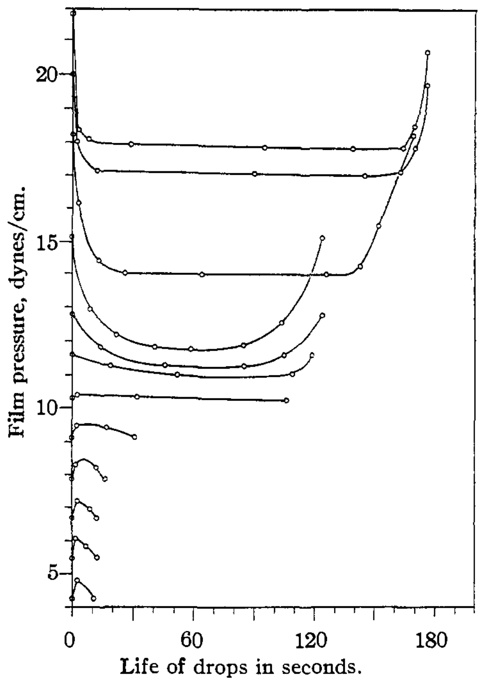

Fig. 2.

perhaps due to the action of gravity as mentioned previously,[2] and a much increased time for evaporation. The latter was undoubtedly due to the increased thickness of the drop or lens, which could not spread as a thin layer. The upper six curves are alike in that they show an initial decrease in pressure followed finally by an increase which again leaves a final pressure very nearly equal to the initial pressure, sometimes less than the initial, but never greater. It is probable that the initial decrease was due to solution of the stearic acid film in the benzene. That this is the cause is indicated by the fact that much surface activity was evident around the periphery of the drop during the time that the pressure was decreasing. The drops rested quietly upon the surface during the time that the pressure remained constant, but activity again became evident as the pressure increased as the last of the benzene evaporated. It was also noted that when the drop or lens of benzene happened to migrate to the edge of the tray, it rapidly spread upon it, the benzene evaporated, and the pressure–area relationships indicated a loss of film (left upon the edges of the tray). Drops of benzene forced to the edge of the tray at pressures such that no initial decrease was noted spread on the edges and evaporated without measurable loss of film. The increase in pressure near the end of the life of a drop represented by any one of the upper six curves was due to the redeposition of the stearic acid as the benzene evaporated.

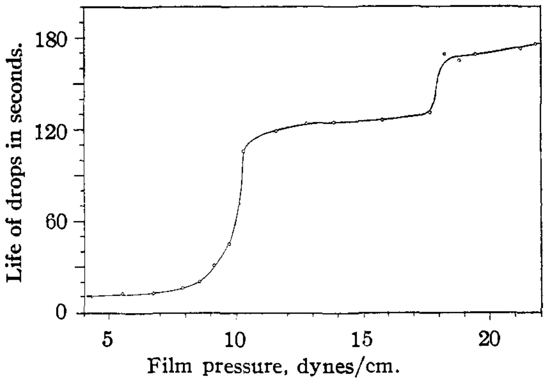

Fig. 3.

As the initial film pressure at which the drops of benzene were added increased, the time required for the drops to evaporate increased. The increase in time was gradual until the initial pressure of the film was the spreading pressure of benzene, when a sudden and rather large increase was noted. At this pressure or above no thin layer of benzene is formed—all of the material remaining as a lens of visible thickness. This pressure is definite and reproducible to within ±0.1 dyne per centimeter. As the initial pressure was further increased, gradual increases in the life of the drops was noted until a pressure was reached at which a second large increase in drop life was experienced. This is shown in Fig. 2 by the difference in lengths of the horizontal portions of the top three curves as compared with three just below the top three. An equilibrium between the factors causing decrease and increase in film pressure is indicated by these nearly horizontal portions. The sudden increase in time required for evaporation is more clearly shown in Fig. 3, which was constructed from the study of a larger number of drops than are included in Fig. 2. This second large increase corresponds to the abrupt decrease in the changes in pressure shown in Fig. 1 in connection with points 5 and 5′, and 6 and 6′ on curves A and B. It seems possible that some rather abrupt change in the shape of the drop must occur at these pressures analogous to the change from a film to a lens experienced at the spreading pressure. It was noted that at about the pressure at which the second increase in drop life took place, the drop ceased to focus light from above on the bottom of the tray. This suggests greater curvature and a shorter focal length. It may be that the drop of benzene was forced out of contact with the water to a position on top of the stearic acid. No sudden change in appearance, other than that noted in regard to the focal length, was observed. Of course more stearic acid would be expected to dissolve in the benzene at higher film pressures and this would slow down the rate of evaporation. One would hardly expect a sudden and large increase in life of drop to result from this cause.

The pressure at which this second increase took place was not as definite and reproducible as the spreading pressure. At the present time it is not possible to enumerate the factors which determine the pressure at which the increase in time of evaporation occurs.

At the higher pressures it was noted frequently that the film pressure after evaporation was not as great as the initial pressure before the drop was added. This difference, larger than the normal, slow decrease which occurs with films under such pressures, indicates loss of film material. This was probably due to the failure of some of the dissolved stearic acid to take its place in the film as the benzene evaporated. Deposits of film material were visible as the three values plotted in curve A of Fig. 1 above 20 dynes per centimeter were obtained.

Attempts were made to measure the minimum pressure at which appreciable solution of stearic acid in the benzene took place. As the film pressure was gradually increased, added drops of benzene were blown to the edge of the tray with a current of air. Observations were then made to discover whether or not a loss of film material had occurred. The critical film solution pressures thus measured were not very reproducible, but in a number of trials values between 10.8 and 11.4 dynes per cm. were indicated.

Summary

The times required for uniform drops of benzene to evaporate from monomolecular films of stearic acid in different states of compression on water have been measured.

The changes in pressure of the monomolecular films due to these spreading and evaporating drops have been determined.

Attempts have been made to explain some of the rather interesting observations in terms of changes in shape and condition of the drops, and in terms of solution of film in the drops and its subsequent redeposition.

LINCOLN, NEBRASKA RECEIVED JULY 18, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, FORDHAM UNIVERSITY]

Preparation of Palladium and Platinum Synthetic High Polymer Catalysts and the Relationship between Particle Size and Rate of Hydrogenation

BY LOUIS D. RAMPINO* AND F. F. NORD

Investigations in the field of catalytic hydrogenation have led to the development of a new type of colloidal catalyst. The present paper describes the preparation of palladium and platinum catalysts in which synthetic high polymers are used as protective colloids. The particle size of the protective colloid and the rate of hydrogenation have been related by studies of polyvinyl alcohol (PVA) in various degress of polymerization as the protecting agent. Also, studies have been made of catalysts with PVA solutions which have been subjected to freezing to determine their activities in relation to the change of particle size deduced from earlier work.[1] Gold numbers of the various preparations have been determined. The use of PVA and polyacrylic acid as protective colloids is limited to water and water–alcohol mixtures. For hydrogenations in organic solvents we have therefore applied the polymer of methyl methacrylate (MMA) and that of the methyl ester of polyacrylic acid (PAME).

Apparatus.—The apparatus consisted essentially of a system of burets, a specially constructed hydrogenation

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* From part of a thesis submitted to the Graduate School of Fordham University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1941. (Present address, Frick Chemical Laboratory, Princeton University.) A report on this work was presented at the St. Louis meeting of the American Chemical Society, April, 1941.

(1) F. F. Nord, *Naturwissenschaften.*, **24**, 481 (1936); L. Holzapfel and F. F. Nord, *Ber.*, **71**, 1217 (1938); *Biodynamica*, **3**, No. 57 (1940); F. F. Nord, *Ergebn. Enzymforschung*, **2**, 23 (1933).