tion of carbon dioxide at the same percentage dehydration at temperatures of 34.5, 61.2 and 100°. This behavior is explained as due to the collapse of the crystal skeleton when the last fractions of the water are removed.

Slightly dehydrated chabasite exhibits a pronounced specificity of adsorption toward hydrogen, oxygen and carbon dioxide. This behavior is explained on the assumption of several limiting pore sizes and of differing extents of the corresponding inner surfaces.

CAMBRIDGE, MASS.
RECEIVED AUGUST 19, 1936

NOTES

The Ethyl Esters of Triiodophenoxyacetic Acids and Potassium Triiodophenoxyacetate

BY T. C. DANIELS AND R. E. LYONS

Several hitherto undescribed triiodophenoxy substitution products of ethyl acetate have been prepared because of their possible opacity to x-rays. The procedure followed was similar to that used by Hewett, Johnson and Pope[1] in preparing tribromophenoxyacetic esters. A mixture of 0.05 mole of triiodophenol, with equivalent quantities of sodium and of ethyl mono-, di- or trichloroacetate, dissolved in 50 cc. of absolute alcohol, was heated on a water-bath for two, three and one-half, or seven hours, respectively, and then poured into 250 cc. of cold water. The monophenoxy derivative, after two recrystallizations from alcohol, was obtained in 40% yield as colorless silky crystals; the diphenoxy, after two recrystallizations from chloroform (in which iodine was liberated slowly) as colorless needles. Attempts to secure the triphenoxy derivative in crystalline form were unavailing, only a yellow, amorphous mass being obtained.

The mono-substituted ester was hydrolyzed incompletely by heating with 30% aqueous potassium hydroxide for several hours. The reaction mixture was poured into water, filtered and the free acid precipitated by dilute hydrochloric acid. Saponification of the di- and tri-substituted esters does not occur under similar conditions.

TABLE I

Phenoxyacetate	M. p., °C.	Formula	Iodine, % Calcd.	Iodine, % Found
Ethyl triiodo-	128.5	$C_{10}H_9O_3I_3$	68.27	67.98
Ethyl ditri-iodo-	160.0	$C_{10}H_{10}O_4I_6$	74.02	73.77
Ethyl tri-tri-iodo-	208–211[a]	$C_{22}H_{11}O_5I_9$	76.23	76.06
Potassium triiodo-	211 (free acid)	$C_8H_4O_3I_3K$	67.07	66.63

[a] Decomposition point.

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RECEIVED OCTOBER 12, 1936

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[1] Hewett, Johnson and Pope, *J. Chem. Soc.*, **103**, 1630 (1913).

The Effect of Helium on the Kinetics of the Thermal Decomposition of Acetaldehyde

BY C. J. M. FLETCHER

The extent to which organic molecules decompose by way of a free radical and chain mechanism, or by a simple rearrangement, has been a matter of considerable debate. Although there is an increasing body of experimental evidence which indicates that free radicals and chain processes do exist in the decomposition of such molecules, there is still the alternative that molecular rearrangement can compete with the chain mechanism often to its virtual exclusion. Acetaldehyde is a substance for which a chain mechanism has been proposed,[1] and it has been suggested that the kinetics of its chain decomposition in the presence of free radicals produced either photochemically,[2] or by the thermal decomposition of azomethane,[3] support such a mechanism. However, the concentration of free radicals present,[4] the influence of small amounts of nitric oxide,[5] and the catalysis of acetaldehyde by diethyl ether[6] do not support this hypothesis.

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[1] F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[2] Leermakers, *ibid.*, **56**, 1537 (1934).

[3] Allen and Sickman, *ibid.*, **56**, 2031 (1934).

[4] Patet, *Z. physik. Chem.*, **B32**, 294 (1936).

[5] Staveley and Hinshelwood, *J. Chem. Soc.*, 812 (1936).

[6] Fletcher and Rollefson, THIS JOURNAL, **58**, 2129 (1936).

The effect of inert gases on the rate of reaction also indicates that the decomposition does not follow the chain mechanism:

$$\begin{array}{rlccc} CH_3CHO & \longrightarrow CH_3 + CHO & k_1 & E_1 & (1) \\ CH_3 + CH_3CHO & \longrightarrow CH_4 + CH_3CO & k_2 & E_2 & (2) \\ CH_3.CO & \longrightarrow CH_3 + CO & k_3 & E_3 & (3) \\ 2CH_3 & \longrightarrow C_2H_6 & k_4 & E_4 & (4) \\ 2CH_3 + M & \longrightarrow C_2H_6 + M & k_5 & E_5 & (5) \end{array}$$

but rather the direct rearrangement

$$CH_3CHO \longrightarrow CH_4 + CO \qquad k_6 \qquad E_6 \qquad (6)$$

for whereas at temperatures above 440°, the recombination of methyl radicals is mainly a homogeneous reaction which takes place partially at ternary collisions so that the rate of the chain reaction is retarded by helium,[7] the thermal decomposition of acetaldehyde itself is accelerated by nitrogen,[8] and by helium (Table I).

TABLE I

TEMPERATURE 552°

$p_{\text{Acet.}}$, mm.	p_{He}, mm.	$t_{1/3}$, sec.	$t_{1/2}/t_{1/3}$	Increase in $1/t_{1/3}$, %
93.9	429	148	1.97	11
82.0	375	160	1.95	10
96.4	...	163	1.94	..
83.0	...	175	1.93	..

The last column of Table I gives the increase in rate (as determined from values of the time taken for the pressure to increase by one-third of the initial pressure of acetaldehyde) in the presence of helium compared to the rate for the same initial pressure of pure acetaldehyde.

The results with helium were obtained with the same experimental procedure as that for which it was found that the rate of the chain decomposition in the presence of ethylene oxide was retarded by about 10% at 441° for a 2:1 helium ratio.[7] As the heterogeneous recombination of methyl radicals decreases with temperature, the acceleration given in Table I cannot be accounted for by the inert gas preventing the diffusion of radicals to the walls. Neither can it be explained on the chain mechanism by an increase in the rate of production of methyl radicals such as might occur if reaction 1 were second order; for the initial rate of the chain mechanism is

$$-(\mathrm{d}p/\mathrm{d}t) = p^{(n/2)+1}\, k_2 \sqrt{k_1/[k_4 + k_5\,(\mathrm{M})]} \qquad (1)$$

where n is the order of reaction 1, so that to explain the observed order of approximately 1.5, Reaction 1 has to be first order.

As the chain mechanism competes so ineffectively with the direct rearrangement, it may be assumed that its over-all energy of activation, $E_{\text{ald.}}$, is considerably higher. If the variation with temperature of the recombination of free radicals at ternary collisions can be neglected, then, from equation 1, $E_{\text{ald.}} = E_2 + {}^1/_2(E_1 - E_4)$. Values of $(E_2 - {}^1/_2E_4)$ may be obtained from the decompositions induced by azomethane and ethylene oxide; from the results with azomethane, Allen and Sickman[3] derived the value 13,800 cal. on the assumption, which is probably justified,[9] that all the azomethane decomposes to give free radicals. With ethylene oxide the fraction of molecules which gives free radicals is approximately 14%;[7] if the temperature independent factors are the same for both types of decomposition, such a proportion would be obtained if the energies of activation differ by about 3000 cal., *i. e.*, that for the production of free radicals would be approximately 56,000 cal. Making a calculation similar to that for azomethane, $(E_2 - {}^1/_2E_4)$ is therefore 13,500 cal., in good agreement with the value from azomethane. Thus $E_{\text{ald.}} \simeq {}^1/_2E_1 + 13{,}700$ cal., so that for the chain mechanism to have a larger energy of activation than that actually observed (50,000 cal.[10] or 45,700 cal.[11]), the energy of activation (E_1) for the breaking of the C–C bond must be closer to 80,000 cal. than to the value of 70,000 cal. assumed by Rice and Herzfeld.

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[7] Fletcher and Rollefson, THIS JOURNAL, **58**, 2135 (1936).

[8] Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **A128**, 91 (1930).

[9] O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

[10] Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933).

[11] Letort, *Compt. rend.*, **199**, 1617 (1934).

THE CHEMICAL LABORATORY
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RECEIVED SEPTEMBER 15, 1936

The Standard Electrode Potential of Silver

BY J. J. LINGANE AND W. D. LARSON

The value for the standard potential of the silver electrode, Ag | Ag$^+$ (a = 1), given by Lewis and Randall[1] is −0.7995 v., whereas the value given in the "International Critical Tables"[2] is −0.7978 v. Both of these values apparently are based on the measurements of Noyes and Brann[3] on cells involving liquid junction potentials. Evaluation of the standard potential of the silver electrode from these measurements

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[1] Lewis and Randall, "Thermodynamics," McGraw Hill Book Co., Inc., New York, 1923, p. 414.

[2] "International Critical Tables," Vol. VI, p. 333.

[3] Noyes and Brann, THIS JOURNAL, **34**, 1016 (1912).

necessitates the use of the standard potential of the calomel electrode, and the difference between the two values given above apparently is due to the revision of the accepted value of the standard potential of the calomel electrode.

We wish to call attention to a simple unambiguous method by means of which the standard electrode potential of silver may be calculated from the standard potential of the silver–silver chloride electrode, $\mathrm{Ag} \mid \mathrm{AgCl(s)},\ \mathrm{Cl^-}\ (a = 1)$, and the activity product of silver chloride. The relation between the standard potential of the silver–silver chloride electrode, E^0_{AgCl}, the activity product of silver chloride, K, and the standard potential of the silver electrode $E^0_{\mathrm{Ag,\,Ag^+}}$, is given by the thermodynamic equation

$$E^0_{\mathrm{AgCl}} = E^0_{\mathrm{Ag,\,Ag^+}} - (RT/F)\ln K \qquad (1)$$

The value of E^0_{AgCl} has been determined by several investigators[4] from measurements of the cell $\mathrm{H_2} \mid \mathrm{HCl,\ AgCl(s)} \mid \mathrm{Ag}$. A critical examination of the data of these authors has led us to believe that the measurements of Carmody, who used quartz cells and was the only one of these investigators who was able to obtain very concordant results in extremely dilute solutions, are the most reliable. By graphical extrapolation Carmody obtained the value −0.2223 v. for E^0_{AgCl}. We have recalculated the value of E^0_{AgCl} from Carmody's data for the three most dilute solutions (0.0007280, 0.0005518 and 0.0003288 m) by application of the limiting law of Debye and Hückel. This leads to the equation

$$E^0_{\mathrm{AgCl}} = -E_{\mathrm{cell}} - \frac{RT}{F}\ln m^2 + 2 \times 0.5045\,\frac{RT}{F}\,S^{1/2} \qquad (2)$$

in which S is the total ionic strength of the solution corrected for the solubility of silver chloride. This equation leads to the same value of E^0_{AgCl} for each of the three most dilute solutions, namely, −0.2222 v. at 25°. We consider this to be the most reliable value of E^0_{AgCl}, and it is in excellent agreement with the value −0.2221 v. estimated by Randall and Young.[5]

The activity product of silver chloride has been determined recently by Brown and MacInnes[6] by a highly precise electrometric titration method. They found a value of K equal to 1.721×10^{-10} at 25°, and this result is apparently reliable to a few tenths of one per cent.

By substituting these values into equation (1) we obtain for the standard electrode potential of silver at 25°

$$E^0_{\mathrm{Ag,\,Ag^+}} = -0.2222 + 0.05913\log(1.721 \times 10^{-10}) = -0.7996\ \mathrm{v.}$$

The close agreement between this result and the value given by Lewis and Randall is remarkable in view of the fact that the value calculated above is based on entirely independent measurements by different investigators. This result therefore constitutes strong evidence in favor of accepting the value −0.7996 v. as the standard potential of the silver electrode, rather than the value −0.7978 v. given in the "International Critical Tables."

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RECEIVED AUGUST 1, 1936

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[4] (a) Noyes and Ellis, This Journal, **39**, 2532 (1917); (b) Linhart, *ibid.*, **41**, 1175 (1919); (c) Scatchard, *ibid.*, **47**, 708 (1925); (d) Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926); (e) Carmody, This Journal, **54**, 188 (1932).

[5] Randall and Young, *ibid.*, **50**, 989 (1928).

[6] Brown and MacInnes, *ibid.*, **57**, 459 (1935).

Beta-Octyl Thiocyanate

BY W. GORDON ROSE AND H. L. HALLER

In the course of studies on the relative toxicity to insects of optical isomers of secondary alkyl thiocyanates, the results of which will be reported elsewhere, occasion has been had to prepare the dextro and levo forms of beta-octyl thiocyanate (alpha-methylheptyl thiocyanate). By the action of phosphorus tribromide (138.0 g.) on dextro-beta-octanol (66.0 g.), $[\alpha]^{20}\mathrm{D}$ +9.70° homogeneous, $[\alpha]^{20}\mathrm{D}$ +11.88° in ethanol (c = 5.67), there was obtained 81.3 g. of beta-octyl bromide, $[\alpha]^{20}\mathrm{D}$ −32.15° homogeneous, $[\alpha]^{20}\mathrm{D}$ −45.30° in ethanol (c = 5.99). The latter (81.0 g.), on being refluxed in 100 cc. of methanol with 45.0 g. of potassium thiocyanate, yielded 51.7 g. of beta-octyl thiocyanate, b. p. 98.5–99.0° at 4 mm., d^{20} 0.919, $n^{20}\mathrm{D}$ 1.4635, $MR\mathrm{D}$(obsd.) = 51.30, $MR\mathrm{D}$(calcd.) = 51.09, $[\alpha]^{20}\mathrm{D}$ +51.7° homogeneous, $[\alpha]^{20}\mathrm{D}$ +59.1° in ethanol (c = 5.06). *Anal.* Calcd. for $\mathrm{C_9H_{17}NS}$: C, 63.08; H, 10.01; N, 8.18. Found: C, 63.14, 63.17; H, 10.02, 10.08; N, 8.44, 8.32.

Beta-octyl thiocyanate has been obtained previously by the interaction of beta-octyl-*p*-toluenesulfonate and potassium thiocyanate.[1] The beta-octyl sulfonate was obtained on oxidation of the corresponding sulfinate, which in turn

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[1] Kenyon, Phillips and Pittman, *J. Chem. Soc.*, 1081 (1935).

was obtained from beta-octanol and *p*-toluenesulfinyl chloride. Starting with a dextro-beta-octanol, $[\alpha]^{20}_{5893}$ +9.48° homogeneous, $[\alpha]^{20}_{4359}$ +22.40° in ethanol (c = 4.992), Kenyon and his co-workers obtained, through this series of reactions, a levo-beta-octyl thiocyanate, $[\alpha]^{20}_{5893}$ −71.41° homogeneous, $[\alpha]^{20}_{5893}$ −64.68° in ethanol (c = 5.010), $n^{17^\circ}_{\mathrm{D}}$ 1.4651, $d^{20^\circ}_{4}$ 0.795.

In the series of reactions used by the writers a dextrorotatory octanol yielded a dextrorotatory thiocyanate, while in the procedure used by Kenyon a levo-octyl thiocyanate was obtained from a dextrorotatory octanol. Since an asymmetric carbon atom is involved in both series of reactions, the difference in the results may be explained by the occurrence or absence of the Walden inversion.

The refractive index of the thiocyanate prepared by the writers agrees with that reported by Kenyon and his co-workers, indicating that the compounds are of the same degree of chemical purity. The density of the writers' compound, however, was 0.919, whereas Kenyon reported 0.795.

The molecular refraction of beta-octyl thiocyanate, calculated from the revised values of Eisenlohr for the atomic refractions[2] and employing 13.21 for the thiocyanate radical, is 51.09. The observed molecular refraction for the writers' compound, obtained with the Lorentz-Lorenz formula, is 51.31, whereas with the values for refractive index and density reported by Kenyon 59.31 is obtained.

These results indicate that the value for the density found by the writers is closer to the true value than is that found by Kenyon, *et al.* Since the specific refraction (homogeneous) is dependent on the density, this value is also subject to revision.

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[2] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Aufl. 5, Bd. 2, Julius Springer, Berlin, 1923, p. 985.

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A Stopcock Substitute

By Walter C. Schumb and H. Irving Crane

In the course of a certain investigation in this Laboratory it was found necessary to devise a means of interrupting the flow of a benzene solution. A stopcock could not be used, since the ordinary organic stopcock lubricants are readily attacked by benzene, and the reactivity of the solute toward moisture or reactive hydrogen made the use of certain other types of lubricant, such as phosphoric acid, out of the question. The device shown in the diagram is an adaptation of Stock's stopcock for gases [*Ber.*, **58,** 2058 (1925)].

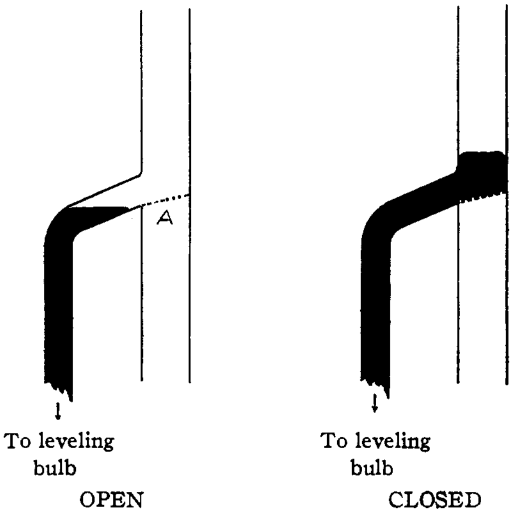

Fig. 1.

The device, constructed of Pyrex glass, consists essentially of a fritted glass plate (A) (80 mesh), so placed that mercury can be flowed over it at will by means of a suitable leveling bulb.

Obviously the device is applicable to any liquid of not too high viscosity, which does not attack mercury. The high surface tension of mercury prevents any of it passing through the fritted plate.

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The Rearrangement of Alkyl Aryl Thioethers

By Wendell H. Taylor

In a recent study of the reaction between aromatic mercaptals and formaldehyde, the author[1] postulated a rearrangement of formaldehyde diaryl mercaptals involving the migration of the —CH_2 group from sulfur to the benzene nucleus, with regeneration of the —SH groups. Such a change would be essentially similar to the rearrangement of the alkyl aryl thioethers and it was therefore of interest to investigate such thioether rearrangements under conditions comparable to those under which the analogous oxygen com-

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[1] W. H. Taylor, This Journal, **57**, 1065 (1935).

pounds isomerize, and comparable also to the conditions of the above-mentioned mercaptal reaction.

The rearrangement of two allyl aryl thioethers has previously been reported,[2] both, however, involving "pyrolysis" of the compounds at their rather high boiling points (215–264°) in the absence of solvents or rearranging agents. The present communication reports briefly on the rearrangement of allyl *p*-tolyl sulfide, *s*-butyl *p*-tolyl sulfide and *s*-butyl phenyl sulfide in the presence of zinc chloride–acetic acid reagent which has been found[3] a satisfactory rearranging medium for the oxygen ethers at temperatures as low as 112°.

In the three cases studied the thioether underwent partial rearrangement to one or more alkyl-substituted thiophenols, obtained finally by precipitation as lead mercaptides. Simultaneously a scission of the thioether molecule appeared to take place, fairly large amounts of allene and butylene being evolved. This is in sharp contrast to the non-production of unsaturated gases reported[4] in thioether and oxygen ether pyrolysis, but corresponds exactly to the observations of Sprung and Wallis. The presence of thiophenol and *p*-thiocresol as the other scission products was indicated by the high percentage of lead found by analysis of the total lead mercaptide precipitate, and by interpolation an approximate ratio of rearrangement product to decomposition product was obtained. Although a part of the thiophenols set free in the reaction suffered oxidation to disulfides and could not be weighed as lead mercaptides, thereby rendering an accurate estimate of the extent of the rearrangement impossible, the isomerization of —CH$_2$—S—R to R(CH$_2$—)SH was definitely established.

For assistance with a part of the experimental work the author wishes to thank Messrs. W. A. Bastedo, Jr., and R. W. Storer.

Experimental

The thioethers were prepared in good yields by heating the appropriate alkyl bromide for twenty-four hours at 110–120° with the sodium salt of thiophenol or *p*-thiocresol. Allyl *p*-tolyl sulfide had the properties described by Hurd; *s*-butyl phenyl sulfide, b. p. 104–105° (25 mm.); *s*-butyl *p*-tolyl sulfide b. p. 135–138° (22 mm.). All were colorless liquids of not unpleasant odor, giving no reaction with alcoholic lead acetate solution. The zinc chloride–acetic acid reagent contained 10 g. of fused zinc chloride in 26 cc. of solution.

In a typical experiment 20–30 cc. of the zinc chloride solution was heated for three hours at 135–150° in a flask provided with a dropping funnel and connected *via* a reflux condenser to a gas buret. After the air thus had been displaced partially, 2.5–10 g. of the thioether was run in and the heating continued for twenty-four hours more, by which time the evolution of gas had practically ceased. By passing steam into the reaction flask all remaining gas was easily driven over into the buret, the contents of which were tested from time to time during the reaction period. The heavy, brownish product which remained in the flask was extracted with ether, and the portion of this which then dissolved in warm 95% alcohol was treated immediately with a saturated alcoholic solution of lead acetate. The precipitate of lead mercaptides was filtered off, washed, dried and analyzed for lead by the usual method of gentle ignition followed by treatment with nitric and sulfuric acids to give lead sulfate.

In the rearrangement of allyl *p*-tolyl sulfide, the volume of gaseous product having the properties of allene—odor, inflammability with luminous flame, reaction with bromine water and with mercuric chloride, inertness toward ammoniacal silver nitrate—amounted to 30–60 cc. per gram of thioether originally taken, the yield decreasing as the reaction temperature was raised from 135 to 150°. The orange lead mercaptide precipitate, presumably a mixture of the lead salts of *p*-thiocresol and 2-allyl-4-methyl thiophenol, gave on analysis 40.2–40.8% Pb. Calcd. for $Pb(SC_6H_4CH_3)_2$: Pb, 43.4; calcd. for $Pb(S\cdot C_6H_3\cdot C_3H_5\cdot CH_3)_2$: Pb, 38.9. The value obtained by analysis would correspond to a mixed mercaptide precipitate containing from 57.5–71% of the lead salt of 2-allyl-4-methyl thiophenol.

In the case of the butyl aryl ethers similar results were obtained. The gaseous product had the properties of butylene but was produced in smaller quantity—from 25–37 cc./g. of the butyl phenyl sulfide, and from 10–15 cc./g. of the butyl *p*-tolyl sulfide. Only in the case of the former was a quantitative analysis of the mercaptide precipitate made. The heavy yellow powder was found to contain 41.8% Pb. Calcd. for $Pb(SC_6H_5)_2$: Pb. 48.7; calcd. for $Pb(SC_6H_4C_4H_9)_2$: Pb, 38.5. This would correspond to a mixture of the two mercaptides containing 69% of the lead salt of *s*-butyl thiophenol.

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RECEIVED AUGUST 8, 1936

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[2] Hurd and Greengard, THIS JOURNAL, **52**, 3356 (1930).

[3] Sprung and Wallis, *ibid.*, **56**, 1715 (1934).

[4] Hurd and Webb, *ibid.*, **58**, 943 (1936).

The Spinning Top Ultracentrifuge and the Sedimentation of Small Molecules

BY J. W. WILLIAMS AND C. C. WATSON

In recent articles McBain and O'Sullivan[1] have discussed their development of the air-driven spinning top as transparent ultracentrifuge. As we read these reports we cannot escape the feeling that a certain pronouncement in them requires further analysis. In the "Communication" a

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[1] McBain and O'Sullivan, THIS JOURNAL, **57**, 780, 2631 (1935).

"fortunate accident" is mentioned which made it possible "to observe the sedimentation velocity of a boundary in aqueous solution of mercuric chloride: $s = 0.891 \times 10^{-13}$ cm./sec./dyne; theory $= 0.890 \times 10^{-13}$." Later, in the definitive article, McBain and O'Sullivan make the claim that they have recorded for the first time the sedimentation velocity of an ordinary molecule (mercuric chloride), this as a footnote to the statements "For sedimentation equilibrium of ordinary molecules, powers ranging from 100,000 to 1,000,000 times gravity are essential. Still higher powers will be required for observing their sedimentation velocity."

It has seemed worth while to examine this extremely important claim, which is made more striking because of the remarkable agreement between theory and observation (about 0.1%) which is reported. Such examination is extremely difficult because definite information is lacking as regards the speed at which the rotor was turning, how the position of the boundary was observed and located at the ends of the several intervals of time during the centrifuging, how the distances from the center of the cell were measured, how the absence of convection effects was proved, what was the concentration of the solution and the temperature of the cell used in the experiment, how long the centrifuging was continued, etc. However, by making calculations which involve the dimensions of the apparatus, the rotor speeds, and strengths of the materials of construction mentioned in other parts of the longer article, it is concluded that their sedimentation power was not over 350,000 times gravity. For a molecule of weight and density of mercuric chloride in water at ordinary temperatures, one may calculate that the actual sedimentation rate with such centrifugal force would be of the order of 1 mm. per hour.

With the apparatus as described and with the assumption of technique and evaluation of the data according to the methods developed by Svedberg, it is highly improbable that such a rate could be measured with the precision claimed. Also, a serious difficulty is that the back diffusion would so blur the boundary that the distance of travel of the latter in any ordinary interval of time would be hard to estimate. Experiments of Pedersen[2] made in the Svedberg laboratory may be cited in this connection. Working with aqueous solutions of mercuric chloride and at 350,000 times gravity, this investigator was able to establish equilibrium in a cell with liquid column about 5 mm. in height after something like seven hours of centrifuging. However, no mention is made by Pedersen of the observations of the velocity of the sedimentation.

Actually, in view of the very careful Pedersen experiments and several statements contained in the article in question, there may be some doubt that a true sedimentation velocity was observed. In addition to the two sentences quoted above, McBain and O'Sullivan define an ultracentrifuge as being "any centrifuge of low or high power in which convection does not occur, and in which it is possible to measure any redistribution of the contents." Again in referring to the behavior of a rotor which is described as having several advantages (speed, uniformity of temperature, strength) over the one in which the experiment in question took place, there is the statement "With the driving air arbitrarily thermostated to within ±0.02° and the room temperature controlled, the same rotor will sometimes sediment molecules as small as purified egg albumin (molecular weight about 35,000)."

It is a matter of some surprise to find the theoretical sedimentation velocity constant for mercuric chloride molecules in aqueous medium expressed to three significant figures when no temperature is specified. The value of the constant varies considerably with temperature because the viscosity of the solvent is involved. The variation amounts to approximately 2% per degree in aqueous solution at ordinary centrifuge temperatures. For mercuric chloride the theorectical sedimentation constant expressed to two significant figures is 0.73 at 20°, 0.82 at 25° and 0.89 at 30°. The temperature of the cell during the experiment was not determined with precision.

Since the records of the experiment and the calculation for the corresponding theoretical specific sedimentation velocity for mercuric chloride are so incomplete, we are impelled to suggest that a further account of the work be presented before it can be given serious consideration as the first measurement of the sedimentation velocity of an ordinary molecule.

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RECEIVED MARCH 31, 1936

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[2] Pedersen, *Z. physik. Chem.*, **A170**, 53 (1934).

Addendum to the Note of Williams and Watson

BY JAMES W. MCBAIN

I do not consider that the note by Williams and Watson calls for any detailed comment. The two sentences published by McBain and O'Sullivan, one sentence in a preliminary communication and the other single sentence in a footnote in a paper of eleven printed pages entitled "The Development of the Air-Driven Spinning Top as a Transparent Ultracentrifuge," still appear to be ample notice of the physical phenomenon that was observed, on November 15, 1934, with the old circular cell whose use was discontinued that year. The cell contained pure water and a crystal of mercuric chloride. Sufficient of the latter dissolved in the lower portion of the cell and then through an accident of convection currents, the absorbing material ($HgCl_2$) was sedimented downward again with a fairly sharp boundary as shown by the photographs and microphotometer photographs, moving 0.102 cm. in 8400 seconds at 108,600 r. p. m. with an average radius of 1.054 cm., giving an observed $S = MD \times (1 - V)/RT = 0.890 \times 10^{-13}$, which, as a mere scientific curiosity, agreed with the value predicted. The precise agreement is of course fortuitous and should not have been expressed to three significant figures, as is obvious to anyone who has any knowledge of an ultracentrifuge.

Professor Williams has acknowledged Dr. O'Sullivan's statement that the sedimentation force was 138,000 times gravity, but Williams and Watson prefer to state "it is concluded that it was not over 350,000 times gravity."

McBain and O'Sullivan stated that this result was an accident and that in the ordinary course, where convection does not occur, a higher order of magnitude of centrifugal force than that in any existing ultracentrifuge anywhere today would be required to obtain sedimentation velocities of such small molecules regularly.

It is entirely a matter of individual opinion as to whether any significance whatsoever attaches to this photographed and microphotometered observation, and Williams and Watson are convinced on the basis of their experience that none does. We still think that it did offer an actual semi-quantitative measurement.

As regards the fourth paragraph of the note of Williams and Watson devoted to discussing the state of development of our air-driven ultracentrifuge as described at the April, 1935, meeting of the Society, it is only necessary to say that our statements were carefully made and stand accordingly as referring to the now superseded models as developed at that time; and that the appreciable modifications and the very simple temperature control in the later model referred to in the footnote by H. J. Fouts inserted at the end of that paper in the final proofs have resulted in uniform success in sedimenting smaller protein molecules such as carbon monoxide hemoglobin—as was, for example, demonstrated at the Western Protein Conference, June 6, 1936. There appears now to be no reason why any sedimentation velocity or equilibrium observable in the Svedberg ultracentrifuges, or the equally good air-driven models now developed, for example, at the Rockefeller Institute for Medical Research [see for example *J. Exptl. Medicine*, **64**, 39 (1936)], or the model supplied by the Sharples Specialty Company of Philadelphia should not also be capable of quantitative study in the McBain–O'Sullivan–Fouts transparent ultracentrifuge. All parts of this cell are easily kept at any desired *constant* measured temperature within 0.02°. All forms of the air-driven ultracentrifuge appear to be in process of still further rapid improvement.

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Chemical Nature of δ-Follicular Hormone

BY O. WINTERSTEINER, E. SCHWENK, H. HIRSCHMANN AND B. WHITMAN

In 1932 Schwenk and Hildebrandt[1] reported the isolation from the urine of pregnant mares of a new oestrogenic substance, isomeric with oestrone (theelin), which they designated δ-follicular hormone. Wintersteiner, Schwenk and Whitman[2] subsequently showed that this substance (m. p. 209°) was not a ketone, but a dihydroxy compound. Recently larger amounts of crude phenolic fractions from mares' urine were separated in the laboratories of the Schering Corporation into ketones and alcohols. The alcoholic portion was worked up for δ-hormone at Columbia University. Our present experience with material of this type makes it appear doubtful whether the earlier preparations represented a chemical individual,

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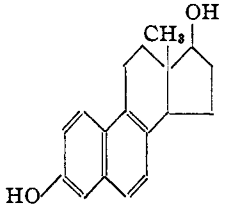
[1] Schwenk and Hildebrandt, *Naturw.*, **20**, 658 (1932).

[2] Wintersteiner, Schwenk and Whitman, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1087 (1935).

a possibility discussed in the first publication. Fractional crystallization yielded an apparently homogeneous product which did not change its melting point (226° corr.) on repeated recrystallization from various solvents. However, the analytical composition and specific rotation varied with different preparations ($[\alpha]_D$ +31 to +37°). The preponderant constituent of these mixtures appears to be a molecular compound consisting of two components. Only one component forms a picrate, and this property as well as its stronger acidic character enabled us to isolate this component in pure form.

The new compound melts at 215–217° and has the composition $C_{18}H_{20}O_2$ (calcd.: C, 80.55; H, 7.52; found: C, 80.53, 80.47; H, 7.61, 7.52); $[\alpha]^{25}_D$ −4.7° (0.7% in dioxane). A di-*p*-nitrobenzoate (m. p. 250–252° corr.) and a monobenzoate (m. p. 203–205° corr.) have been prepared. The compound gives the color reactions originally attributed to the δ-follicular hormone.[1,3] Its absorption spectrum coincides with that of equilenin. Our measurements on equilenin reveal two new bands in addition to those found by Dirscherl and Hanusch,[4] namely, at 2310 Å., log ε 4.78, and at 2920 Å., log ε 3.58.

The monobenzoate was oxidized with chromic acid to a ketone which gave no depression of its melting point (223° corr.) when mixed with equilenin benzoate. The dihydroxy compound (m. p. 217°) is therefore dihydroequilenin.



Contrary to the rule, established for other oestrogenic compounds, that reduction of the C_{17} keto group to carbinol enhances the physiological activity, the dihydroequilenin isolated from urine possesses only about one-half of the potency of equilenin. On the other hand, David[5] found that the oily product which he obtained by reduction of equilenin with sodium was about three times as potent as equilenin. The possibility that our diol differs from the potent oestrogenic diols, obtained by reduction, in the configuration of the C_{17} hydroxyl group will be investigated. Whether the high potency originally reported for the δ-hormone resides in the other, as yet unidentified, component of the molecular compound (m. p. 226°) or in other diols present in the impure preparations, remains to be determined.

We wish to express our sincere thanks to Dr. A. Girard of Paris for sending us samples of equilenin and its benzoate for comparison.

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RECEIVED NOVEMBER 12, 1936

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[3] Schwenk and Hildebrandt, *Biochem. Z.*, **259**, 240 (1933).

[4] Dirscherl and Hanusch, *Z. physiol. Chem.*, **233**, 13 (1935).

[5] David, *Acta brevia Neerl.*, **4**, 63 (1934).

Phenylmercuric Fluoride

BY GEORGE F. WRIGHT[1]

The recent discovery[2] of mercuric fluoride as a new fluorinating agent recalls the investigation in this Laboratory of phenylmercuric fluoride. This preparation was incidental in the study of the relative strengths of C–Hg and Hg–X bonds in organomercuric halides. According to our knowledge of organomercurials the tendency toward the dissociation reaction $2RHgX \rightleftharpoons R_2Hg + HgX_2$ decreases in the order HgI > HgBr > HgCl. It was hoped that the introduction of fluorine would so stabilize the Hg–X bond as to favor the primary reaction $RHgX \longrightarrow R— + HgX$ which, it is considered, accounts for the interconversion possible with compounds like furyl and thienylmercuric halides containing more reactive, though unfortunately less stable, radicals.[3] The compound did not, however, fulfil these expectations. Instead of reacting with acetyl chloride to give acetophenone, acetyl fluoride was formed as easily as from mercuric fluoride.[2] Likewise when the compound was pyrolyzed at a temperature lower than that required to decompose diphenylmercury, only the latter substance, and no diphenyl, was produced.

In connection with the assertion of Henne and Midgley that pure mercuric fluoride cannot be prepared by treating mercuric oxide with aqueous hydrofluoric acid it may be significant that treatment of such a solution with phenyldiazonium fluoride, and subsequent treatment with copper, produced no trace of phenylmercuric fluoride.

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[1] National Research Fellow in Chemistry.

[2] Henne and Midgley, THIS JOURNAL, **58**, 884 (1936).

[3] Steinkopf and Bauermeister, *Ann.*, **403**, 50 (1914); Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

I wish to thank Professor E. P. Kohler for suggestions offered during this investigation.

Experimental

Phenylmercuric Fluoride.—A solution of 40.6 g. (0.17 mole) of freshly precipitated silver oxide and 14 g. (0.35 mole) of 50% hydrofluoric acid in 400 cc. of water was shaken for five hours with 78 g. (0.25 mole) of phenylmercuric chloride, previously moistened with ethanol. The solid was filtered off and extracted with 400 cc. of boiling ethanol. After a small amount of precipitation by cooling, the solution was decanted and concentrated *in vacuo*. The residue was extracted with boiling ethanol and filtered. The cooled solution yielded 32 g. of phenylmercuric fluoride, m. p. 170°, or 43% of the theoretical. The chlorine-free compound was soluble in hot alcohol, hot xylene and hot chloroform and was crystallized from the latter solvent for analysis (m. p. 171°). It was insoluble in carbon tetrachloride, ethyl acetate, ether and hot acetone. The extracted silver chloride from the reaction mixture contained much unreacted phenylmercuric chloride; no doubt the yield can be increased by a longer period of reaction.

Anal. Calcd. for C_6H_5HgF: C, 24.27; H, 1.70. Found: C, 24.25; H, 1.99.

Reaction with Acetyl Chloride.—When 2.96 g. (0.01 mole) of phenylmercuric fluoride was refluxed with 1.57 g. (0.02 mole) of acetyl chloride, the acetyl fluoride was evolved immediately through the reflux condenser. After five hours the reaction was poured into iced sodium carbonate solution. No mercuric oxide precipitated. The solid was filtered off and crystallized from xylene to weigh 2.80 g. and melt at 257°. This 90% yield of phenylmercuric chloride was substantiated by mixed melting point.

Diphenylmercury.—When phenylmercuric fluoride was slowly destructively distilled at 200° under 10 mm. only diphenylmercury, and no diphenyl, could be found in the distillate.

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RECEIVED SEPTEMBER 14, 1936

COMMUNICATIONS TO THE EDITOR

METAL ION ACTIVATION IN ENZYMATIC CATALYSIS. ARGINASE

Sir:

Recent investigations [Hellerman, Perkins, and Clark, *Proc. Nat. Acad. Sci.*, **19**, 855 (1933); Hellerman and Perkins, *J. Biol. Chem.*, **107**, 241 (1934); Bersin, *Z. physiol. Chem.*, **220**, 209 (1933)] support the idea that reversible chemical actions upon substituent thiol groups of certain enzymes (urease, papain, etc.) may account largely for their reversible inactivations by oxidation and by silver ion, phenylmercuric hydroxide, etc. However, the enzyme, arginase [Hellerman and Perkins, *J. Biol. Chem.*, **112**, 175 (1935)], was found to be little sensitive to phenylmercuric hydroxide, and most readily activated, not by reduction in the usual sense but rather by the use of reduced ions of the transition elements, manganese, cobalt or nickel, as well as ferrous ion, which had been associated previously with arginase activation. This, and other evidence cited, was considered to point strongly to metal coördination as a factor not merely in arginase activation but actually in the functioning of the enzyme itself. For example, dissociable, labile enzyme-substrate intermediates might be constructed by the "binding" to a metal ion of both enzyme and substrate through donor groupings of each. If so, an effective metal ion should alter the activity–*p*H curve of arginase in a characteristic way.

We have now studied the effect of such ions upon the arginase–arginine reaction in buffers of widely varying *p*H values but having approximately constant ionic strength ($\mu = 1$). Activity–*p*H curves constructed from the data clearly show characteristic differences. Liver-arginase action is enhanced greatly by nickelous and especially cobaltous ion from *p*H 5 to 7.7; activation by manganous ion is not significant below *p*H 6.7. The optima for cobaltous, nickelous and manganous ion are, respectively, *p*H 7.5 to 7.7, 6.7 to 7.7 and 10 as compared with the optimum for our arginase, without added metal, 7.7 to 9.0. The variations may be considered in relation to the corresponding stabilities of the coördination complexes of these ions with substituted ammonias. For example, we ascertained (by a potentiometric titration method) that the dissociation constants of the complex ions derived from *d*-arginine with cobaltous, nickelous