

Fig. 3.—Per cent. of maximum deposition of radiosilver on platinum as a function of time at several temperatures.

to a pH value of 2.0 with perchloric acid could not be reproduced. However, all curves were of the type as shown in Figs. 2 and 3.

TABLE I
DEPOSITION ON VARIOUS METALS AT 27°

Metal	1st run		2nd run	
	Max. removed, ^a %	Half-time, min. ^b	Max. removed, ^a %	Half-time, min. ^b
Zn	75	25
Al	65	20
Pb	45	15	60	10
Sn	15	15	25	30
Cu	85	15	75	30
Ni	85	15	35	25
Pt	75	10	70	15

^a Given to the nearest 5%. ^b Given to the nearest 5 min.

Discussion

The anomalous metal foil potentials measured in perchloric acid at a pH value of 3.0 are in reasonable agreement with those measured in 0.1 M hydrochloric acid,³ in 0.125 M nitric acid,⁴ and in dilute hydrofluoric acid,⁵ except for silver. A value of -0.42 v. has been obtained in this investigation as compared to previously measured values of -0.29 v. in 0.1 M hydrochloric acid and -0.26 v. in 0.125 M nitric acid. It is interesting to note that none of the anomalous silver foil potentials are even close to the deposition potential of tracer radio-silver, which is reported as -0.77 v.²

Table I indicates that it is difficult to draw any conclusion relating either high rates of deposition or large percentages deposited to electropositive character in the metals. It seems that the lack of reproducibility in the various runs might be assigned to differences in the surfaces of the individual metal foils. Since determinations of anomalous metal potentials can be duplicated using different foils that have undergone pretreatment with flint paper, while deposition determinations cannot be reproduced using similarly prepared foils, one questions whether there is any direct relation between the anomalous potentials and the deposition behavior. Camarcat, Bouissieres and Haissinsky,⁵ from their data on the spontaneous deposition of

protactinium, conclude that there is more of a relation between deposition behavior and the standard electrode potentials of the metals than between the deposition behavior and the anomalous potentials. This investigation shows no apparent relation to either potential.

The results of the surface effect studies seem to indicate that the surface plays an important role in the deposition behavior. Just exactly what this role is cannot be concluded from the present work. Perhaps differences in adsorption of silver ions or atoms onto the surfaces may be involved. Numerous authors⁷ have treated this possibility from a theoretical viewpoint, and conclude that this is a likely explanation.

The data from the deposition on the platinum foil indicate that the maximum amount deposited decreased as the pH value went from 2.0 to 7.0. This effect may be due to the tendency of tracer silver to form radiocolloids as the pH of the solution is increased.⁶ With increases in temperature, the rate of deposition onto platinum increased. The fact that hot concentrated nitric acid was necessary to remove the radiosilver from the platinum indicates that the silver has been deposited as an atom and probably does not exist in the form of an adsorbed ion.

Some investigators have hypothesized that the lack of reproducibility in spontaneous deposition behavior was due to the absence of any intentionally added ions corresponding to the metal foil under consideration. To test this hypothesis in the case of silver, depositions onto copper from solutions containing macro amounts of copper(II) ion were run. The results could not be duplicated, thus lending no support to the hypothesis.

(7) M. Haissinsky, "Electrochimie des substances radioactives et des solutions extrêmement diluées," Herman and Cie, Paris, 1946, pp. 27-34; J. Byrne, L. Rogers and J. Greiss, *J. Electrochem. Soc.*, **98**, 447, 452, 457 (1952); M. Haissinsky, *Experientia*, [4] **8**, 125 (1952).

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Acylhydrazones of *o*-Oxy- and *o*-Aminoaldehydes and Ketones as Tridentate Complexing Agents

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In the course of previous works on chemical reactions of complexes¹ a number of acylhydrazones of salicylaldehyde, 5-bromosalicylaldehyde, *o*-oxynaphthaldehyde, *o*-oxyacetophenone and *o*-aminobenzaldehyde were prepared. These products are able to react as tridentate groups and to yield, with nickel, bicyclic and polynucleate complexes.

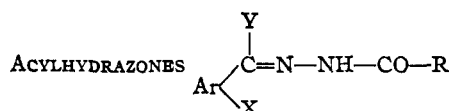
The data obtained for a series of acylhydrazones are given in Table I.

Experimental

Preparation of the Acylhydrazones.—The solution of aldehyde or ketone and acylhydrazines (1 mole:1 mole) in alcohol was heated under reflux on steam-bath for about one hour and cooled. Water was often added in order to obtain a larger yield of crystalline precipitate. The products were purified by recrystallization from 95% or dilute alcohol.

(1) L. Sacconi, *THIS JOURNAL*, **74**, 4503 (1952); *Z. anorg. allgem. Chem.*, **277**, 176 (1953); *Gazz. chim. ital.*, in course of being printed.

TABLE I



Y = H, CH₃; X = OH, NH₂; R = (CH₂)₁₂-CH₃, C₆H₅, CH₂-C₆H₅, C₆H₄NO₂; Ar = C₆H₄, C₁₀H₆.

Hydrazone	Formula	M.p., °C.	Crystals	Nitrogen, %	
				Calcd.	Found
Salicylaldehyde myristyl	C ₂₇ H ₃₄ O ₂ N ₂	104-105	White	8.10	8.23
Salicylaldehyde <i>o</i> -nitrobenzoyl	C ₁₄ H ₁₁ O ₄ N ₃	175-177	Yellow	14.73	15.17
<i>o</i> -Oxynaphthaldehyde myristyl	C ₂₈ H ₃₆ O ₂ N ₂	129-130	Yellow	7.07	7.00
<i>o</i> -Oxynaphthaldehyde benzoyl	C ₁₈ H ₁₄ O ₂ N ₂	211-212	White	9.74	9.75
<i>o</i> -Oxynaphthaldehyde fenylacetyl	C ₁₉ H ₁₆ O ₂ N ₂	204-206	Yellow	9.20	9.12
<i>o</i> -Oxyacetophenone benzoyl	C ₁₅ H ₁₄ O ₂ N ₂	180-181	White	11.06	10.92
<i>o</i> -Aminobenzaldehyde myristyl	C ₂₇ H ₃₆ ON ₃	103-104	White	12.16	12.00
<i>o</i> -Aminobenzaldehyde benzoyl	C ₁₆ H ₁₃ ON ₃	180-181	Yellow	17.57	17.67
<i>o</i> -Aminobenzaldehyde fenylacetyl	C ₁₆ H ₁₅ ON ₃	164-165	Yellow	16.59	16.50
Salicylaldehyde picolinyl	C ₁₃ H ₁₁ O ₂ N ₃	171-173	White	17.42	17.37
<i>o</i> -Oxynaphthaldehyde picolinyl	C ₁₇ H ₁₃ O ₂ N ₃	189-190	Yellow	14.43	14.35
<i>o</i> -Oxyacetophenone picolinyl	C ₁₄ H ₁₃ O ₂ N ₃	184-186	White	16.47	16.35
<i>o</i> -Aminobenzaldehyde picolinyl	C ₁₃ H ₁₂ ON ₄	216-218	Yellow	23.33	23.42
Salicylaldehyde nicotinyl	C ₁₃ H ₁₁ O ₂ N ₃	175-177	White	17.42	17.57
<i>o</i> -Oxynaphthaldehyde nicotinyl	C ₁₇ H ₁₃ O ₂ N ₃	252-253	Yellow	14.43	14.53
<i>o</i> -Oxyacetophenone nicotinyl	C ₁₄ H ₁₃ O ₂ N ₃	183-185	White	16.47	16.43
<i>o</i> -Aminobenzaldehyde nicotinyl	C ₁₃ H ₁₂ ON ₄	208	Yellow	23.33	23.28
5-Bromosalicylaldehyde nicotinyl	C ₁₃ H ₁₀ O ₂ N ₃ Br	216-217	Yellow	13.12	13.09
Salicylaldehyde isonicotinyl	C ₁₃ H ₁₁ O ₂ N ₃	244-245	White	17.42	17.48
<i>o</i> -Oxynaphthaldehyde isonicotinyl	C ₁₇ H ₁₃ O ₂ N ₃	155-157	Yellow	14.43	14.15
<i>o</i> -Oxyacetophenone isonicotinyl	C ₁₄ H ₁₃ O ₂ N ₃	235-237	White	16.47	16.43
<i>o</i> -Aminobenzaldehyde isonicotinyl	C ₁₃ H ₁₂ ON ₄	232-233	Yellow	23.33	23.20
5-Bromosalicylaldehyde isonicotinyl	C ₁₃ H ₁₀ O ₂ N ₃ Br	251-252	Yellow	13.12	13.10

All hydrazones, except those of *o*-aminobenzaldehyde, are soluble in dilute sodium hydroxide and in aqueous ammonia with yellow color.

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Chemical Interactions of Amino Compounds and Sugars. VIII.¹ Influence of Water²

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This Laboratory has been concerned with a rather extended study of the color-producing (browning) reaction between a reducing sugar (such as D-xylose) and an amino acid (such as glycine, in excess) in dilute aqueous solution. From an applied food product standpoint, most of these browning reactions occur in relatively low water concentrations and such environments have been recently studied extensively by Lea and associates.³ While our immediate program is not concerned with these applied aspects, it was never-

(1) Previous communication in this series: M. L. Wolfrom, Doris K. Kolb and A. W. Langer, Jr., *THIS JOURNAL*, **75**, 3471 (1953).

(2) This paper represents research undertaken in cooperation with the Quartermaster Institute for the Armed Forces under Contract No. DA11-009-qm-13294 with The Ohio State University Research Foundation (Project 477), and has been assigned number 420 in the series of papers approved for publication. The views or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Department of Defense.

(3) C. H. Lea and R. S. Hannan, *Biochem. et Biophys. Acta*, **3**, 313 (1949); **4**, 518 (1950); V. M. Lewis and C. H. Lea, *ibid.*, **4**, 532 (1950); C. H. Lea, R. S. Hannan and D. N. Rhodes, *ibid.*, **7**, 366 (1951); R. S. Hannan and C. H. Lea, *ibid.*, **9**, 293 (1952).

theless considered of interest to investigate the parameter of water concentration in our model system. To this end solid mixtures, each containing D-xylose and glycine in 1:5 molar ratio, were heated at 65°, under nitrogen and with mechanical stirring, with various proportions of water. The degree of color formation was determined by measuring the optical density at 490 m μ at a suitable standard dilution after heating periods of four, six and eight hours. The results are plotted in the accompanying figure. Below the abscissa value of about 18.6 (65% water) the reactions were heterogeneous. The degree of coloration increases with time but follows the same

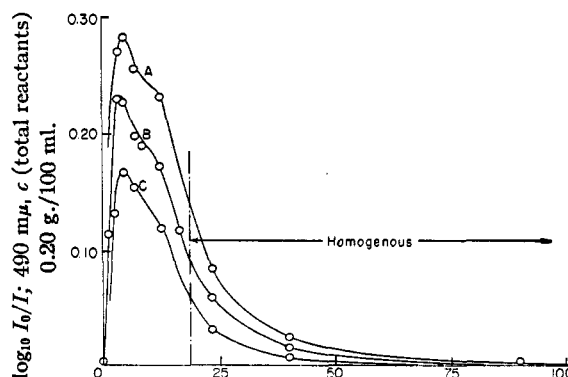


Fig. 1.—Browning of D-xylose-glycine (6.00 g.: 15.00 g. or 1:5 molar ratio) mixtures mechanically stirred (except at 0-1.8 on abscissa) at 65° under nitrogen at various water ratios: curve A, 8 hr. reaction time; curve B, 6 hr.; curve C, 4 hr.; Lumetron (Model 402E) photoelectric colorimeter; 1-cm. cell.