

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Rate of Solution of Zinc in Acids

BY CECIL V. KING AND MORRIS SCHACK

In a previous paper from this Laboratory,¹ it was shown that when a zinc cylinder is rotated in a solution of an acid containing certain "depolarizers," the rate of solution increases continuously up to a peripheral speed of at least 35,000 cm./min. It has been proposed by a number of investigators that at sufficiently high stirring speeds in such systems, the rate should become independent of the stirring speed, provided that the rate of attainment of chemical or other equilibrium on the immediate surface of the solid be not too high. However, no authentic case of the type considered here has been found in which the observed solution rate does not increase continuously with the rate of stirring.

In the experiments reported below, zinc cylinders were rotated with peripheral speeds up to 163,000 cm./min. with no indication that the rate of solution would become constant at any attainable speed.

No study was made in the previous investigation of the effect of changing the concentration of "depolarizer" on the rate of solution of zinc.¹ It was shown that with enough potassium nitrate or hydrogen peroxide present, zinc and cadmium dissolve in dilute hydrochloric and acetic acids at nearly the same rate as magnesium and marble, and that the effect of impurities in the zinc is minimized. It was naturally assumed that at some lower concentration of depolarizer, the rate would be dependent in some way on the concentration of the latter. This point has been studied in detail, as described below, and additional oxidizing agents also.

The effect of adding high concentrations of sodium chloride and of sodium acetate to the acetic acid solutions was also studied.

Experimental

For the experiments at higher peripheral speed, zinc cylinders of various diameters from 2 to 4 cm. and lengths 2.54 down to 1 cm. were rotated by a motor normally running at 1750 r. p. m. with built-in speed increasing gears of ten to one ratio. The ends of these cylinders were protected by rubber washers and hard rubber nuts; in three liters of

solution in a rectangular glass vessel, with several baffle plates, it was found possible to attain a peripheral speed of 160,000 cm./min. without too much cavitation. Immediately before each experiment the surface of the zinc was polished with 0000 emery paper, cleaned, and the cylinder weighed. After the run it was washed, dried at room temperature and weighed.

1.—Table I merely showed that the unimolecular equation applies in the potassium nitrate solutions at unusually high rotational speed.

TABLE I

RATE OF SOLUTION OF ZINC CYLINDER
2.55 cm. high, 1.93–1.94 cm. diameter, 15000 r. p. m., 25°,
in 3 liters of 0.01 *M* acetic acid, 0.0215 *M* sodium acetate,
0.05 *M* potassium nitrate (initial concentrations)

<i>t</i> , min.	<i>x</i> , mg.	<i>A</i> , sq. cm.	<i>k</i>
5	69	15.54	2.84
10	132	15.54	2.79
20	250	15.50	2.84
30	359	15.50	2.92
50	524	15.46	2.95
	(981)

The constant was calculated from the expression

$$k = \frac{2.3V}{At} \log \frac{a}{a-x}$$

Since the reduction product of the nitrate is unknown, and in fact several products are probably formed, the value of *a* is uncertain; it should perhaps be somewhat lower than 981 mg. Use of a lower value, however, would not seriously change the constancy of the values for *k*.

2.—Tables II, III and IV and Fig. 1 record the experiments with varying rotational speed. At very high speeds the rates are not easy to check accurately and the relative smoothness of curves 2 and 3 compared to curve 1 shows the results of experience with the apparatus. Since acetic acid gave no evidence of an approaching maximum rate, the acetic acid-acetate buffer of curve 2 was used, in the hope that the lower hydrogen-ion concentration would permit a maximum to be reached. Finally the much weaker acid *p*-nitrophenol (*K* = 7 × 10⁻⁸) was chosen. Still weaker acids are of questionable desirability because of the probable formation of insoluble coatings on the metal from hydrolysis of the zinc salts.

(1) King and Braverman, *THIS JOURNAL*, 54, 1744 (1932).

TABLE II

THE RATE OF SOLUTION OF ZINC

In 0.01 *M* acetic acid, 0.05 *M* potassium nitrate, 3 liters solution, 25 ± 0.5°. Expts. 1-15, length of cylinder 2.55 cm., diameter 1.99-1.95 cm. Expts. 16-27, length 1.27 cm., diameter 3.66-3.64 cm.

Expt.	<i>P</i> , cm./min.	<i>x</i> , mg., 5 min.	<i>k</i>
1	18,750	26.6	1.04
2	24,880	32.2	1.26
3	31,000	38.0	1.50
4	37,320	44.5	1.76
5	43,325	51.5	2.05
6	50,000	55.0	2.17
7	56,260	62.5	2.48
8	61,890	66.0	2.64
9	68,080	72.0	2.89
10	75,000	78.5	3.14
11	80,040	87.5	3.57
12	86,200	92.5	3.78
13	92,350	94.0	3.84
14	98,000	99.5	4.14
15	104,140	113.0	4.71
16	91,500	89.5	3.92
17	102,900	100.0	4.43
18	103,200	98.0	4.32
19	114,700	110.5	4.93
20	114,700	112.0	4.99
21	126,000	116.0	5.17
22	126,000	115.5	5.15
23	137,500	120.0	5.37
24	137,500	120.0	5.37
25	149,300	131.5	5.90
26	149,300	129.0	5.78
27	163,200	142.5	6.73

TABLE III

THE RATE OF SOLUTION OF ZINC

In 0.01 *M* acetic acid, 0.0215 *M* sodium acetate, 0.05 *M* potassium nitrate, 3 liters of solution, 25°, length of cylinder 1.07 cm., diameter 4.41-4.36 cm.

<i>P</i> , cm./min.	<i>x</i> (5 min.)	<i>k</i>
6,200	7.0	0.303
13,700	14.0	.65
27,500	24.0	1.04
41,200	32.5	1.46
55,000	42.0	1.85
68,900	51.5	2.28
82,750	61.0	2.82
96,500	71.0	3.25
110,400	83.0	3.76
124,400	92.5	4.17
138,550	105.0	4.76
152,400	114.0	5.20

The fact that these curves are smooth to high rotational speeds indicates that vibration, cavitation, air bubbles drawn into the solutions, etc., are of minor importance. A more serious question is that of frictional heating at the zinc surface. These solutions were always adjusted to 25 ± 0.1° at the beginning of the experiment, and sometimes rose in temperature, sometimes fell, as much

TABLE IV

THE RATE OF SOLUTION OF ZINC

In 0.01 *M* *p*-nitrophenol, 0.05 *M* potassium nitrate, 3 liters of solution, 25°, length of cylinder 0.98 cm., diameter 4.39-4.37 cm.

<i>P</i>	<i>x</i> (10 min.)	<i>k</i>
41,750	25.0	1.14
41,750	24.5	1.16
55,150	30.0	1.41
68,900	39.5	1.82
82,880	47.5	2.21
96,550	53.5	2.42
110,100	63.0	2.96
123,850	71.0	3.34
137,000	79.5	3.73

as 0.5 or 0.6°, depending on whether the room temperature was above or below 25°. It is possible that the surface temperature always rose a few degrees; this would cause a consistent error of a few per cent. in the rates.

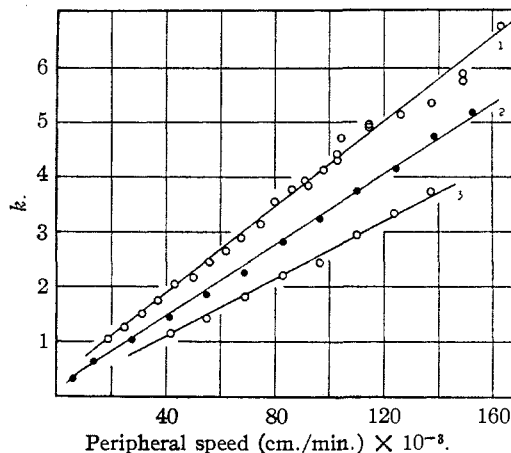


Fig. 1.—The data of Tables II, III and IV: 1, acetic acid; 2, acetic acid buffer; 3, *p*-nitrophenol.

The linearity of the rate curves seems to be of hydrodynamical rather than chemical significance; that is, what we may call a "stirring factor" is linear with peripheral speed above *ca.* 10,000 cm./min. With a stationary piece of metal and a rotating stirrer, the corresponding "stirring factor" would not be linear. The exponent would probably depend on the size and shape of the stirrer used.

3.—Since the addition of relatively small concentrations of sodium acetate to acetic acid did not have the effect of making the rate constant independent of the stirring speed, experiments were carried out with larger additions of sodium acetate, at a constant speed, as shown in Table V and Fig. 2. If the chemical rate of hydrogen ion and nitrate reacting with zinc is very high, that of

TABLE V

RATE OF SOLUTION OF ZINC

In 0.01 *M* acetic acid, 0.025 *M* potassium nitrate, one liter of solution, 25°, length of cylinder 2.54 cm., diameter 1.99–1.97 cm., 5000 r. p. m., *x* = milligrams dissolved in 5 min.

<i>C</i> _{salt} , <i>M</i>	<i>x</i> (NaCl)	η_0/η	<i>x</i> (NaC ₂ H ₃ O ₂)	η_0/η
0	36.8	1	36.0	1
0.1	37.4	0.98
.25	36.9	.97	28.5	0.91
.5	35.1	.95	23.3	.85
1.0	34.7	.92	19.6	.72
1.5	32.1	.87	15.4	.63
2.0	30.0	.84	10.8	.57
2.5	28.7	.81		
3.0	27.0	.78		

undissociated acetic acid and nitrate much lower, it appeared that complete repression of the hydrogen ion might make it possible to measure the chemical rate with the acid molecules.

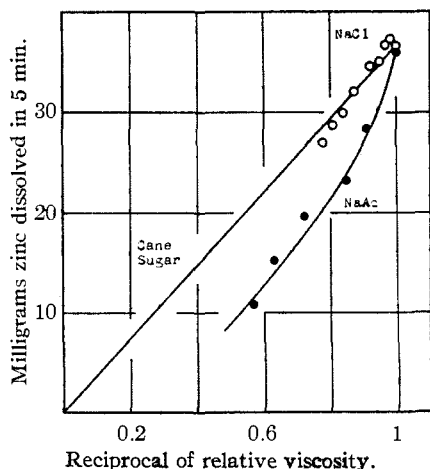


Fig. 2.—The data of Table V.

Sodium acetate of a high degree of purity was used for these experiments, so that the acetic acid concentration would not be altered. In preliminary experiments less pure sodium acetate was adjusted to the correct *pH* before use. Since enough salt was added to change the viscosity several per cent. comparative experiments were made with added sodium chloride, and the rates are plotted against the reciprocal of the relative viscosity, η_0/η . It will be seen that the lower concentrations of sodium chloride have a definite accelerating effect on the rates but higher concentrations retard the rates in almost the same manner as cane sugar. The increase at low concentrations is probably due to the increased ionization and increased diffusion coefficient of the acid. The sodium acetate has a definite retarding effect from the lowest concentrations, much greater than

is warranted by the increasing viscosity. This might be ascribed to a chemical rate, diminished until diffusion is no longer a controlling factor; but we are inclined rather to ascribe it to formation of a film of zinc hydroxide or a basic salt on the zinc surface in these solutions of *pH* around 7.

TABLE VI

RATE OF SOLUTION OF MAGNESIUM

In 0.01 *M* acetic acid, 0.025 *M* potassium nitrate. One liter solution, 25°, length of cylinder 2.54 cm., diameter 1.82 cm., 5000 r. p. m., *x* = milligrams dissolved in 10 min.

<i>C</i> _{salt} , <i>M</i>	<i>x</i> (NaCl)	η_0/η	<i>x</i> (NaC ₂ H ₃ O ₂)	η_0/η
0	24.3	1	24.8	1
0.5	26.4	0.95	20.1	0.85
1.0	25.5	.92	18.4	.72
1.5	23.7	.87	14.9	.63
2.0	22.4	.84	13.0	.56
2.5	21.1	.81		
3.0	19.5	.78		
3.5	18.3	.73		

This view is supported by the comparative experiments with magnesium, shown in Table VI and Fig. 3. The accelerating effect of sodium chloride is more pronounced in this case, and the effect of sodium acetate, which does not increase the ionization or diffusion coefficient of the acid, is fully explained by the increasing viscosity. This is in accord with the higher solubility of magnesium hydroxide.

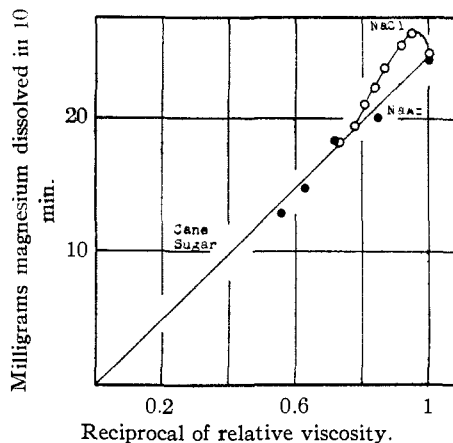


Fig. 3.—The data of Table VI.

4.—Table VII and Figs. 4, 5 and 6 show the effect of changing the concentration of four oxidizing agents with various acetic and hydrochloric acid solutions. At low concentrations the rate is highly dependent on the oxidizing agent concentration and independent of the acid or its concentration (except with the nitrate; see below). The rate is not, however, independent of the particular oxidizing agent. This will be discussed later.

TABLE VII
 MILLIGRAMS OF ZINC DISSOLVED

In 5 min. in one liter of solution, 25°, 5000 r. p. m., length of cylinder 2.54 cm., diameter 1.92-1.83 cm.

Concn. oxid. agent (mpl.)	KNO ₃			H ₂ O ₂		p-Nitrophenol		Quinone	
	0.01 M HAc	0.05 M HAc	0.014 M HCl	0.01 M HAc	0.014 M HCl	0.01 M HAc	0.05 M HAc	0.01 M HAc	0.05 M HAc
0	5.0	5.3	5.1	5.0	5.1	5.0	5.3	5.0	5.3
0.0005	12.5	..	7.5	..
.001	16.5	11.0	17.5	10.0	8.8	19.0	19.0	10.5	10.5
.002	21.2	30.0	..	15.5	..
.003	25.2	21.7	71.0	18.5	19.0	29.5	46.0	21.5	21.0
.004	31.5	..	27.5	..
.005	30.0	35.3	100.0	26.5	25.5	31.5	76.5	33.5	34.5
.008	33.5	36.5	32.5
.01	36.0	..	106.5	35.0	53.0	34.5	142.5	35.5	58.5
.0125	71.5
.015	..	127.0	80.0	37.0	166.5	36.5	88.0
.0175	101.0
.02	36.6	139.5	109.0	34.5	105.0	37.0	168.0	..	116.0
.025	36.4	159.5	113.0	34.5	130.5	36.0	135.0
.03	36.0	157.5	113.5	..	104.0	..	168.0	..	161.0
.035	..	154.5	112.0	..	104.0	171.0
.04	104.5	170.0
.05	36.0	158.5	171.0
Cylinder diam.	1.92	1.91	1.90	1.89	1.88	1.86	1.85	1.84	1.83

Table VIII and Fig. 7 show the effect of keeping constant potassium nitrate concentrations and varying the amount of acetic acid. These curves are quite similar to the others; the rate is first nearly proportional to the acid concentration,

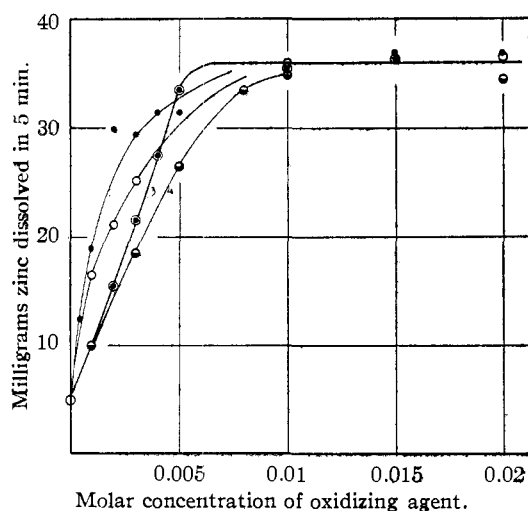


Fig. 4.—Data of Table VII for 0.01 M acetic acid: 1, *p*-nitrophenol; 2, potassium nitrate; 3, quinone; 4, hydrogen peroxide.

nearly independent of the nitrate concentration. Then a maximum rate is reached which is proportional to the nitrate concentration used for each curve.

Discussion

Experiments somewhat similar to those of

Table VII were carried out by Prins,² who measured the rate of solution of zinc and lead in approximately 80% acetic acid, with added nitrobenzene as a depolarizer. He found the rate proportional to the nitrobenzene concentration up to a critical value, above which it still rises less rapidly with lead, but falls off with zinc. Below the critical concentration he finds the rate to be

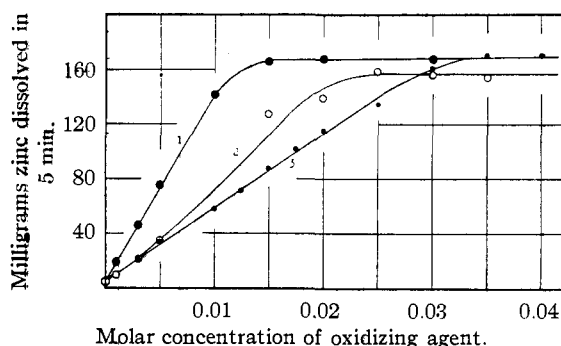


Fig. 5.—Data of Table VII for 0.05 M acetic acid: 1, *p*-nitrophenol; 2, potassium nitrate; 3, quinone.

the same with the two metals, and concludes that the process is controlled by the rate of diffusion of the nitrobenzene to the surface. Above the critical concentration he postulates adsorption of zinc acetate on the surface to explain the subsequent decrease in rate; much less adsorption of lead acetate allows the rate to rise further, though not as rapidly as at low nitrobenzene concentrations.

(2) Prins, *Rec. trav. chim.*, **43**, 942 (1923); **44**, 876 (1925).

TABLE VIII
MILLIGRAMS OF ZINC DISSOLVED

In 5 min. in 3 liters of solution, 25°, 4800 r. p. m., length of cylinder 2.46 cm., diameter 2.18-2.13 cm.

$\text{CH}_3\text{CO}_2\text{H}, M$	0.007M KNO_3	0.005M KNO_3	0.003M KNO_3
0.002	9.0
.003	...	12.0	11.5
.004	16.5
.006	24.0	22.5	21.5
.008	32.5
.009	...	32.5	31.5
.01	35.5
.012	...	42.5	41.0
.015	59.0	52.5	50.0
.018	...	62.5	59.5
.021	75.5	74.0	67.5
.024	80.0
.027	85.5
.03	107.5	100.5	88.5
.033	89.0
.04	145.0	128.0	89.0
.05	170.0	152.0	89.0
.06	193.5	150.0	..
.07	205.0	151.0	..
.08	202.5	152.0	..

In our experiments in very dilute acid there is no evidence of adsorption of the product. The curves indicate a diffusion-controlled rate; with constant acid concentration, the rate is controlled by diffusion of the oxidizing agent at the lower concentrations. The latter reacts as rapidly as it reaches the surface, where acid is present in excess.

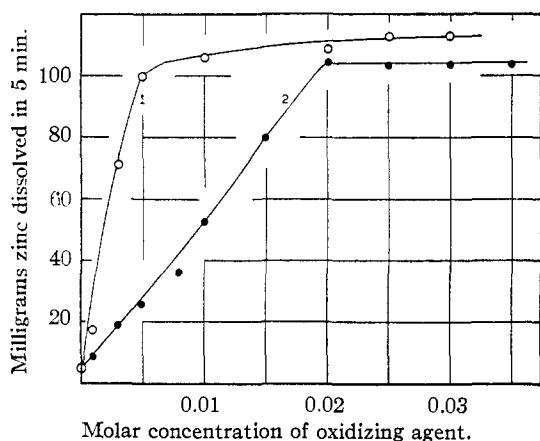


Fig. 6.—Data of Table VII for 0.014 M hydrochloric acid: 1, potassium nitrate; 2, hydrogen peroxide.

With the limited acid concentrations used here, however, a critical concentration of oxidizing agent is reached above which the acid concentration at the metal surface cannot be maintained. An acid concentration gradient is now set up, oxidizing agent is present in excess at the surface

and possesses no concentration gradient, and the process is controlled by the diffusion rate of the acid.

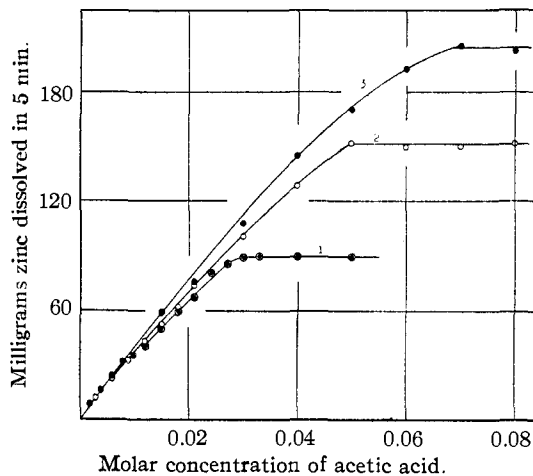


Fig. 7.—Data of Table VIII for potassium nitrate: 1, 0.003 M; 2, 0.005 M; 3, 0.007 M.

The diffusion coefficients of potassium nitrate, *p*-nitrophenol, hydrogen peroxide and quinone (Fig. 4) cannot be far different. The slopes of the curves at low concentrations then depend chiefly on the number of oxidizing equivalents per molecule. The slopes for hydrogen peroxide and quinone (two equivalents) approach each other at low concentrations, although they diverge at higher concentrations. The slope for the nitrophenol is much steeper (six oxidizing equivalents if it is reduced to aminophenol). The curve for the nitrate indicates that it is reduced to hydroxylamine or ammonium ion at low concentration but at slightly higher concentrations is reduced less.

With a fixed concentration of oxidizing agent, the rate is controlled by the diffusion of the acid, at low acid concentrations. In Fig. 7 it is seen that with nitrate present the rate is not quite independent of the acid concentration, below the critical concentration; this is probably due to a difference in reduction products at each concentration, and would not be true with an oxidizing agent which had only one reduction product. The maximum rate is strictly proportional to the concentration of nitrate, and further the acid concentration at which the maximum rate is attained is proportional to the nitrate concentration.

With the grade of zinc used for these experiments, the rate of solution with the acid alone is appreciable. Likewise an increase in acid concentration after the "maximum" rate for each nitrate

concentration is reached, should lead to a slow rise in the rate. Both these factors, however, are small and do not obscure the issue.

Summary

The rate of solution of zinc cylinders, rotating in various acid solutions with depolarizers present,

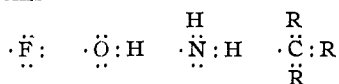
has been measured up to very high rotational speeds. The effect of high concentrations of sodium acetate and sodium chloride on the rate of solution of zinc and magnesium in acetic acid has been studied, and also the effect of varying acid and oxidizing agent concentrations independently. NEW YORK, N. Y. RECEIVED MAY 1, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. V. Aromatic Derivatives of Dixanthyl and *p,p'*-Biphenylene-bi-(diphenylmethyl)

BY HENRY E. BENT AND R. G. GOULD, JR.

Previous papers of this series have shown that sodium adds with about equal ease to many organic free radicals. This result was expected on account of the large electron affinity of triphenylmethyl¹ calculated in the first paper of this series.² Glockler³ has shown that the electron affinity of atoms varies from -28 to +91 kcal. However, if we consider systems involving seven electrons in the outer shell we find the electron affinity remarkably constant. Thus, the values for the halogens are all of the same order of magnitude, ranging from a little over ninety kilocalories for fluorine^{3,4} to seventy-two kilocalories for iodine.⁵ Again if we consider the energy involved in adding an electron to each of the systems



we find that the number of pairs of electrons which are shared apparently affects little the electron affinity. Fluorine gives a value of a little over ninety, OH is reported by Lederle as giving eighty-eight⁶ and the value calculated by one of us for triphenylmethyl is sixty. No value is available for the NH₂ group. We have shown in previous papers of this series that all organic free radicals which we have studied have about the same electron affinity. In these compounds we have not only the same nuclear charge and the

same number of shared electron pairs but also the sharing is always with another carbon atom, which in turn is attached to other carbon atoms. These considerations make it seem very probable that the differences in chemical properties of organic free radicals are not due to differences in the electron affinities of the molecules.⁷

Experimental

Phenylxanthyl Chloride.—Phenylxanthyl was prepared by Dr. W. F. Bruce according to the directions of Gomberg and Cone.⁸ The directions in the literature were followed with the modification that the xanthone was put in an extractor so that the reflux drippings from the boiling ethereal solution of the Grignard reagent slowly dissolved the ketone and carried it into the reaction flask in solution. It was pure white and melted at 159°.

Phenylxanthyl chloride was prepared by the method of Gomberg by dissolving the hydrol in benzene, adding acetyl chloride and dry hydrogen chloride gas. The phenylxanthyl chloride hydrochloride often comes down as an oil but usually turned into a dark red crystalline mass on standing. The crystals, after washing with dry benzene and petroleum ether, were suspended in dry petroleum ether and boiled until a colorless solution was obtained. On cooling, colorless crystals of the phenylxanthyl chloride separated. The material was crystallized several times, great care being taken to prevent hydrolysis. Any hydrogen chloride formed is not liberated but adds to unchanged material to form the highly colored chloride hydrochloride. Pure white, dry chloride turns bright yellow in a few seconds on exposure to air.

Crystallization from benzene involves one-half molecule of benzene of crystallization. The material used in runs one to seven was prepared from this solvent and melted at 86°.

Anal. Calcd. for C₁₉H₁₃OCl·1/2C₆H₆: Cl, 10.70. Found: Cl, 10.60.

(7) Wheland, *J. Chem. Phys.*, **2**, 474 (1934), has come to the conclusion from a theoretical treatment of the resonance energy of free radicals that they should all have the same electron affinity.

(8) Gomberg and Cone, *Ann.*, **370**, 158 (1909).

(1) Kraus and Kahler, *THIS JOURNAL*, **55**, 3537 (1933), have associated the ease of oxidation of sodium triphenylmethyl with a small electron affinity. As the product of the reaction, however, is triphenylmethyl peroxide it would seem that the strength of the carbon oxygen bond is to be held responsible for much of this reactivity.

(2) Bent, *THIS JOURNAL*, **52**, 1498 (1930).

(3) Glockler, *Phys. Rev.*, **46**, 111 (1934).

(4) Mayer and Helmholtz, *Z. Physik*, **75**, 19 (1932).

(5) Sutton and Mayer, *J. Chem. Phys.*, **3**, 20 (1935).

(6) Lederle, *Z. physik. Chem.*, **17B**, 362 (1932).